POROUS TRANSPARENT AEROGELS:
Development of Superinsulating Window Technology
Appendix II

Renewable Energy Branch

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APPENDIX II

A REVIEW ON AEROGELS

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Abstract

Aerogels are extremely porous, low density materials, consisting of inorganic oxides such as silica, alumina, zirconia, stannic or tungsten oxide, or a mixture of these oxides. They have large surface areas and can be translucent as well as transparent, have extremely low thermal conductivities, and fascinating acoustic properties (sound velocities as low as 100 m/s). This review surveys the literature up to the end of 1987 and summarizes the historical background of aerogel development, their production by the sol-gel process, possible drying methods, structural investigations and various novel applications in catalysis, high-energy physics, passive solar energy uses and energy conversions, and low temperature glass formation.

I. Introduction

Aerogels are coherent, porous solids made by the formation of a colloidal followed by removal of the liquid from within the pores of the gel. They are usually of very low density, can be made in large pieces (monolithic structure), and can also be transparent. Aerogels had little practical value until 1974, when Cantin et al. (1a,b) reported on the use of silica aerogels as detectors in Cerenkov radiation. More recently, they have found application as insulation in dual-pane windows (Super Windows) (2), and this has resulted in renewed interest in their production and optimization. Recent reviews on the subject have appeared. Teichner and his group compiled a review in 1976 (3) and Schmitt, in his M.Sc. Thesis on the preparation of silica aerogels, presented an excellent review in 1982 (4). A review of transition metal oxide gels and colloids was presented in 1982 by Livage and Lemerle (5).

This review is concerned primarily with literature (both published and patented) on the preparation of inexpensive monolithic coherent inorganic aerogels which can be used for the production of insulation for super windows. Aerogels made of cerium oxide or other exotic transition metal oxides, though useful in terms of mechanism and methods of preparation, will not be dwelled upon since they would be much more expensive than the silica and aluminum aerogels, and therefore would not warrant large scale production.

II. Early Work

The first report on the preparation of coherent expanded aerogels was published by Kistler in 1932 (6a,b). He clearly showed that

the inorganic gel, when dehydrated under normal conditions, collapses into a powder as a result of the disruption in the pore structure of the gel. However, when the gel is dehydrated under super-critical conditions of temperature and pressure, then the liquid-vapour boundary within the pores of the gel no longer exists and the gels do not collapse on drying. Kistler described the formation of gels of silica, alumina, feric oxide, stannic oxide, tungstic oxide, nickel oxide, as well as several organic materials. Silica gels were made by hydrolysing water glass with hydrochloric acid and allowing the gel to set. It was then washed until the chloride had been removed. When the water in a gel was replaced by ethyl alcohol, Kistler referred to it as an alcogel. The gels were dried by putting them into an autoclave and raising the temperature until the pressure exceeded the critical pressure, then slowly venting the vapours in the autoclave. It was claimed that the aerogels obtained in this manner ranged from transparent to highly opalescent and occupied the same volume as the original alcogel. The density of the aerogel was varied by altering the concentration of silica in the solution. The aerogels can be heated to over 700^{o}C without significant change in appearance. The transmittance of the material decreases when the temperature is increased to 900^{o}C. Thermal conductivities were determined for aerogels in granular as well as cake form. The evacuated samples of granulated aerogels had thermal conductivities of about 0.010 $Wm^{-1}K^{-1}$ at ambient temperatures; this value was much lower for fine granules. A change in the external load did not alter the conductivity significantly. Aerogel tiles showed smaller conductivities at 100 kPa than granular layers but the opposite trend was found at low pressures. From the changes of conductivity with

internal gas pressure above 10 kPa Kistler derived pore size diameters to be of the order of 50 nm. Aluminum acetate, which was subsequently dialyzed to form a 1% solution, was used to form the alumina gel. After gelation, the gel was allowed to dry down to the appropriate concentration. The gel was converted to an alcogel which was subsequently autoclaved to remove the alcohol. Kistler's work is reported in two patents (7,8) which were issued in 1940 and 1941.

III. Gel Preparation and General Aspects

The preparation of aerogels is still more of an art, and much skill is required to achieve a specific end product. The next reported description of the preparation of an aerogel was for use in the IR study of silica surfaces given by Peri in 1966 (9). He hydrolyzed ethylorthosilicate in ethanol with hydrochloric acid and obtained flat gels by allowing the gel formation to occur on a mercury surface. The methanol was slowly replaced by water, and eventually the gel plates were aged for 4 hours in water at 100°C in a closed autoclave. The gels were then slowly transferred back into a methanol solution, which was subsequently vented from an autoclave at conditions of 250-300°C and 1200-1500 psi (8268-10,335 kPa). The plates obtained were flat, transparent and free from cracks, having dimensions of up to 1 x 3 inches (25 x 75 mm) with thicknesses of 1/16 to 1/8 inches (1.6 mm to 3.1 mm). The aerogels had approximate densities of 0.18 g/mL, surface areas of 800 m^2/g, and pore diameters of 250 A. The gels were purified by calcination in oxygen, with evacuation at 600°C.

In 1968, Gilbert Nicolaon submitted his doctoral thesis to the University of Lyon on the subject "Contribution to the study of silica aerogels" (10). He described in detail a variety of processes by which aerogels were made.

Acid and alkali precipitated gels were prepared and characterized for surface area and pore size. The optical transmission properties of the aerogels formed were not reported, since the material was produced for catalytic purposes, and transparency was not of interest to Prof. Teichner, the supervisor of this work. The contents of the thesis are summarized in 5 papers (11a-e), and resulted in the patent issued in 1972 (12). The preparation of alumina aerogels by Teichner and his students has also been described (13). Again, the visual transmission properties of the aerogels are not given, the end uses of the aerogels were for catalytic studies and fundamental adsorption studies of the surface.

Teichner and his coworkers subsequently applied their method of preparing silica aerogels to the detection of Cerenkov radiation (1a,b). The desirability of silica aerogels as Cerenkov detectors is based on the ability to vary the refractive index of the aerogel from 1.01 up to 1.2. This essentially replaces the use of compressed gases as the detection media. The important feature of silica aerogels for Cerenkov detection lies in the transmission properties of the aerogel. This was the first time transparent monolithic pieces of aerogel were made for a specific application. The aerogels were made by the hydrolysis of methylorthosilicate with ammonia in a methanol solution. A large autoclave was used. A detailed description of the preparation is included in the doctoral thesis of Jean Moutel (14). The thesis describes hundreds of experiments where the hydrolysis of the silicate was performed under both acidic, basic and neutral conditions in various solvents to form opaque as well as transparent gels of various characteristics. The densities achieved varied from 0.16 to 0.66 g/mL,

and the refractive index from 1.04 to 1.65. Some optical transmission results are shown in Fig. 1. The factors which influenced the density of the aerogel samples were (a) the nature of the reaction medium, that is, neutral or ammonia for hydrolysis, (b) percentage of the orthosilicate dissolved in the methanol, (c) and the number of moles of water per mole of silicate used to effect the hydrolysis of the methylorthosilicate which was varied from 2 to 6. The percentage of methylorthosilicate was varied between 40 to 100%. Over 70 different combinations of gelling conditions were studied, in most cases in triplicate, giving over 200 samples. Surface areas were determined and thermal-stability was established.

The production of silica aerogels for Cerenkov radiation detectors was also described by the Swedish workers, Henning and Svenson, in 1981 (15). Pieces as large as 18 cm x 18 cm x 3 cm were prepared by an elaborate, detailed procedure. Again, methylorthosilicate was used in methanol with ammonium hydroxide as a hydrolysis catalyst.

Similar aerogels of silica for use as Cerenkov detectors were prepared by the Hamburg group in 1981, with samples as large as 17 cm x 17 cm x 2.3 cm (16). The autoclaves used by these workers were 95 cm deep and 26 cm inside diameter. They were constructed of stainless steel and ordinary steel, with a stainless steel liner. The transmittance of the aerogel samples are shown in Fig. 2, which indicates that a short gelling time is conducive to a high transmittance.

A more detailed account of the experimental methods and results related to Schmitt's work are found in his M.Sc. thesis (4). Schmitt

tested approximately 25 different catalysts to initiate the gel and concluded that fluoroboric acid (HBF_4) was the best, and hydrofluoric acid the second best and most practical catalyst. The kinetics of gelation with hydrofluoric and hydrochloric acid were determined, and the rates of reaction and temperature coefficients evaluated. Steady state thermoconductivity measurements were determined by placing a 2 in x 2 in x 0.4 in (50 mm x 50 mm x 10 mm) slab of aerogel between two chambers, one containing steam and the other water, and observing equilibrium temperature conditions. Schmitt also determined the compression and tensile strength of the aerogels as a function of density. Some results are summarized in Table 1 and 2.

Central to the production of advanced microporous materials is the need for detailed understanding and control of the chemical processes that occur during gel formation (17).

General aspects of the chemistry of metal alkoxides, which make excellent molecular precursors for a variety of inorganic oxides of high purity, have been reviewed (18). The ability of the alkoxides to form homogeneous solutions in a large variety of solvents and in the presence of other alkoxides or metallic derivatives, makes it possible to achieve homogeneity at the molecular level. The parameters governing the hydrolysis of the alkoxides and polymerisation were examined. Modulation of the rheological properties of the sol by controlling the hydrolysis rates enables one to obtain films, coatings, fibers and various body-shaped materials.

The sol-gel process (Fig. 3) describes the transition of a system from liquid, mostly colloidal, into a solid, gel phase. This reaction route can start from two basically different systems - gelation may

proceed due to condensation of colloidal particles (by sol destabilization), cluster growth and crosslinking of polymeric molecules (17).

Hydrolysis: $MOR + H_2O \longrightarrow MOH + HOR$

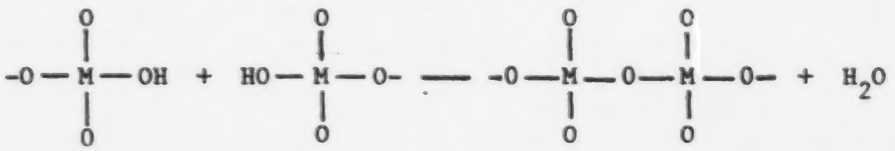
Condensation: $MOR + HOM \longrightarrow MOM + HOR$

$MOH + HOM \longrightarrow MOM + H_2O$

where M = metal or Si

R = alkyl group

Both reactions are catalyzed by acids and bases. However, they also proceed under neutral conditions. The rates for hydrolysis and gelation are strongly pH dependent. To produce fairly homogeneous solids, network-forming components such as Si, main group, early transition metal or lanthanides, usually in the form of alkoxides, should be present. These accomodate the formation of a three dimensional network, typical of a condensation reaction. Acid catalysis leads to a more polymeric form of gel with linear chains as intermediates. Base catalysis yields colloidal gels. Gelation occurs by cross linking of the colloidal particles according to the reaction.



It is evident that hydrolysis and condensation conditions set the primary structures of the gels, and thereby influence further steps. Alkoxides are very sensitive to water, so hydrolysis is possible for a large variety of compounds. Organic network formers or modifiers can be introduced by using organically substituted silico esters as starting compounds, $R'_nSi(OR)_{4-n}$, where R' is an organic functional group and

(OR) is a hydrolysable group. The reaction path, though simple looking, is a complex one, since the single steps are overlapping.

The various factors governing the hydrolysis-polycondensation reactions (18) are: (i) degree of hydrolysis, $h=[H_2O]/[M(OR)_n]$ with $h < n$ leading to fibers, chains, coatings and $h > n$ leading to gels and three dimensional polymers, (ii) nature of the metal and polarity of the M-O-C bond, (iii) n, the number of the alkoxo group -- the rate decreasing with an increase in n, (iv) the nature of the alkoxo group R - this governs the molecular complexity, increases the rate with chain lengthening, controls the sensitivity to hydrolysis (tertiary R > secondary R > primary R, OPh > OR > $OSiR_3$, OPh > ortho $-OC_6H_4X$ $p-OC_6H_4X$), (v) pH, (vi) solvent and dilution and (vii) temperature.

Upon gelation, viscosity increases sharply until the gel point is reached. The structure of the gel, however, may still change i.e. aging depends on temperature, solvent and pH. The effect of pH on the relative reaction rates of hydrolysis and condensation of TEOS is shown in Fig. 4. The condensation reaction starts at a late stage in the case of acid catalysis, but with base catalysis condensation starts relatively early.

Schmidt and Scholze (17) discussed the sol-gel process for non-metallic inorganic materials. Mechanisms of hydrolysis and condensation, and problems associated with maintaining monolithicity were discussed. Mention was made of network modifiers, e.g. the introduction of low-valent cations (such as alkali ions) decreases bond strengthening and leads to lower porosities. Organic network modifiers can also be incorporated into the inorganic network by the sol-gel

process - the organic grouping can be introduced by using an organosilicoester. The sol-gel process can be modified to include a large variety of components including network formers (eg. Ti, Zr, Al) and network modifiers such as organics and dopings. The process therefore has wide material development potential.

Another preparation of a silica aerogel for Cherenkov detector was described using 0.04 M NH_4OH and cooled pre-boiled solutions (19). Several sol-gel systems involving oxides other than SiO_2 have been described: TiO_2/SiO_2(20 -22), SiO_2/GeO_2 (23,24), Al_2O_3(25) and Ti, Zr, Hf, Li (26), V_2O_5(5), WO_3(5).

Recently, Russo and Hunt (27) reported the preparation of a transparent base-catalyzed TEOS aerogel using NH_4OH and NH_4F as catalysts. Russo and Hunt, by using polar nephelometry, reported that the base-catalyzed TMOS system provides better optical quality gels than the acid catalyzed TEOS system.

Tewari (28) and Gowda (29) have prepared silica aerogels using CO_2 as the supercritical fluid. Since CO_2 has a lower critical temperature (T_c = 31°C, P_c = 73 atm) than methanol (T_c = 240°C, P_c = 78 atm) the venting of solvent as a gas is experimentally easier for CO_2. However complete exchange of the methanol for CO_2 must occur.

Italian investigators Pezzo et al (30) studied the influence of the variation of the H_2O/TEOS molar ratio (between 5 - 50) on the microporosity of xerogels produced by hydrolysis of TEOS in the presence of C_2H_5OH and HCl. The gels were allowed to stand at 60°C, and dried in vacuo (P = 0.01 Pa) at 22°C. The adsorption isotherms were determined at -196°C with nitrogen and at 25°C with water. The specific surface area, total pore volume, and the mean radius of mesopores in the

micro-mesoporous silica gels increased with H_2O/TEOS molar ratio, the dependence of the first two parameters being linear. The volume of micropores appeared to be independent of the H_2O/TEOS ratio. Specific surface area of the sample prepared with a H_2O/TEOS molar ratio of 50 reached a value of 665 m^2/g, as determined by the BET method with nitrogen. Recently Avnir and Kaufman (31) produced alcogel from hydrolysis of TMOS without using methanol as a mutual solvent. The alcohol released during the reaction was sufficient to convert the initially biphasic system (H_2O/TEOS = 4:1) into a homogeneous one, resulting in a transparent, porous xerogel after air drying.

The kinetics of silical polymerization was studied by Weres et al. (32). The kinetics of the sol-gel transition was discussed by Klein and Garvey (33), who also obtained (34) monolithic dry gels which were amorphous and transparent. However, densities were high (about 1.6 g/ml) and air drying time was of the order of one month. The object of the work was to obtain a low temperature glass, formed by fixing the gel at high temperature. Much has been reported on the sol-gel route to low temperature glasses.

Abe and Misono published a series of papers summarizing their study of the polymerization of silicic acid (35). They have further shown (36) how it is possible to extract the polymeric acid from water using tetrahydrofuran (THF). The polymer can then be transferred to methanol, and slow evaporation can yield a transparent monolithic gel. No densities were reported. This approach, which starts with water-glass, seems to promise an inexpensive, non-autoclave method of preparing transparent aerogels.

The polymerization of silicic acid, using sodium silicate and tetraethylorthosilicate (TEOS), was studied by Bechtold et al (37) . The kinetics was studied and molecular weights (M_v= 7200 -1.7 x 10^6) determined. The gels were used to prepare fibers which had remarkable properties.

Several papers on diphasic xerogels (38-41) described the preparation of Si/Al, Si/Ag and other mixed oxide systems. The gelling time of a 10% tetramethoxy silane (TMOS) solution in water was shown to be fast almost up to pH 10 (except for pH = 1-3, the gelling is slightly slowed); gelling times were 5 days at pH = 11 and 10 days at pH = 12 (42).

The structure of solid phases in TiO_2 and ZrO_2 gels, obtained from inorganic and organic sources, was studied by Komarneni et al (43). X-ray diffraction (XRD) and selected area electron diffraction (SAED) failed to show any crystalline Ti and Zr hydroxides. Both the gels showed porosity.

Kokubu and Yamane (44) discussed the extraordinary thermal and chemical stability of porous glass-ceramics of the TiO_2-SiO_2 system. Porous glass-ceramics containing both anatase and rutile had thermal expansion coefficients of 40-55 x $10^{-7}K^{-1}$ in the 0-700°C range. They remained porous up to 1000°C, while the pores of high-silica porous Vycor collapsed completely. They attribute the high thermal stability to a high viscosity, resulting from dispersed crystallites of anatase and rutile in the skeleton. Most of the anatase in the skeleton was transformed to rutile during heat treatment at 900°C, but some remained untransformed even after 6 hours.

Tewari, Hunt and Lofftus (45a) described their work at Lawrence Berkeley Laboratories, where they hydrolyzed $Si(OC_2H_5)_4$ with NH_3 and NH_4F catalysts. Ethanol was used as the mutual solvent. A factorial design method was used to choose the experimental parameters, enabling them to reduce the number of experiments required to reach logical conclusions. The concentrations of alkoxide, water, alcohol, and NH_4F and NH_3 were simultaneously varied. The resulting aerogels were either equivalent or better in quality than those produced using the more toxic TMOS as the starting material. Samples were dried using CO_2 at 40°C and 8000 kPa (45b). Light scattering, optical spectroscopy, rheology, system pH, shrinkage during drying, transmission and scanning electron microscopy (TEM, SEM), and surface area measurements were used for sample characterization and optimization.

Zarzycki and Woignier (46) discussed their work, which was performed at CNRS glass laboratory in Montpellier, and involved SiO_2 and other binary SiO_2-B_2O_3, SiO_2-P_2O_5 and ternary system SiO_2-B_2O_3-P_2O_5 aerogels. Aging at room temperature for three weeks and at lower than 50-60°C seemed to improve monolithicity. Ternary systems revealed strong crystallinity which increased with B_2O_3 and P_2O_5 content. The crystalline phase was identified as BPO_4. All of the binary aerogels had interesting optical characteristics. The SiO_2, 20 mol % B_2O_3 gel showed uniform transmission between 12500-50000cm^{-1}, while the SiO_2, 15 mol % P_2O_5 gel cut out at around 35000 cm^{-1} thickness. All of these gels were dried under hypercritical conditions. They discussed how aerogels were used to produce optical quality glass. Optical properties and sintering behavior were studied for the gel-glass transformation.

Brinker et al (47) discussed the synthesis of borate-based aerogels in the binary system, x $Li_2O(1-x)B_2O_3$. $LiOCH_3$ dissolved in methanol was diluted with 2-methoxyethanol and hydrolyzed. The solution was added to the requisite volume of tri-n-butyl borate to obtain molar compositions $xLiO_2(1-x)B_2O_3$ where x varied from 0 to 0.4. Polymer growth in solution was followed by SAXS and the fraction of four-coordinated boron was determined in the original solutions, aged solutions and gels using ^{11}B NMR. Structural information on the molecular scale was obtained from FTIR. The gels were dried under hypercritical conditions using CO_2 at 40°C and 8268 kPa. The aerogel microstructure was examind by SEM. It was concluded that in order to grow stable polymeric species, both a critical hydrolysis ratio and alkali ratio must be exceeded: $[H_2O]/[OR] \geq 0.44$ and $x \geq 0.2$ respectively. Only primary units containing at least one four-coordinated boron appear to be stable in solution. Polymer growth occurs by linkage of these primary units at tetrahedral boron sites. At least one four-coordinated boron is required in B-O-B linkages between primary units. The borate network is very susceptible to dissociation reactions, which promote depolymerization of the network. Since this depolymerization is enhanced at higher temperatures and pressures, amylacetate (T_c = 326.1°C, P_c = 28 atm) was exchanged with liquid CO_2 before SCD (super critical drying). This process had no detectable shrinkage. IR studies indicated that the gel was weakly polymerized compared to glass. Both SEM, TEM micrographs indicated that gelation may occur by a random aggregation of almost spherical polymeric clusters, which is similar to gelation in base-catalyzed systems. The agglomeration of such silica

spheres is responsible for the structure of opals (48).

Though Teichner had reported on the preparation of alumina aerogels as early as 1970, he gave no consideration to the transparency of the materials so produced (13). In 1975, Yoldas reported on the preparation of transparent porous alumina aerogels made by hydrolysis of aluminum alkoxides (49,50). It is interesting to note that the preparations by Yoldas do not involve venting of the solvent in an autoclave, but rather the direct thermal heating of the transparent gel to high temperatures after an initial drying period. Typical transmittance curves are shown in Fig. 5 for a 2 mm thick sample. The samples had 63% open volume and were prepared from an alumina sol (51). The Yoldas work is summarized in two patents dealing with the formation of the transparent alumina material (52,53).

IV. Structural Aspects

Various modern analytical techniques have been employed to study the structure of aerogels. For pore size distribution, Hg-porosimetry and adsorption/desorption of N_2 at low temperatures have been used. Results indicate that aerogels have a pore-diameter distribution which extends from the nm to m range.

A high-resolution electron microscopic study of silica aerogels has shown that the aerogel network consists of particles 10 nm in diameter. ESCA and Auger spectroscopy showed the particles to be pure SiO_2 (54,55).

Tiwari et al (56) described their investigations of micro structural properties of transparent silica aerogels with SEM and TEM. Both acid catalyzed and base catalyzed TEOS and TMOS aerogels were

investigated. The gels were dried both by high and low temperature (alcohol and CO_2) super critical drying. Optical transmission spectra (Fig. 6) in the UV/VIS/NIR (200-3200 nm) region were presented. Transmittance improved on heating up to 500°C. The rising part of the curve between 200-800 nm is due to scattering; after heating to 300°C, the curve is shifted to lower wavelengths. This is attributable either to a decrease in pore-size or a decrease in the average index of refraction. By analyzing the data for Rayleigh scattering, the characteristic size of the scatterer was found to be 8 nm, which is larger than the value of 5 nm for particle size obtained from TEM studies. Acid catalyzed aerogels were found to be denser than the base-catalyzed aerogels. Their pore structure reflected this while the particle sizes were similar. The average void size was calculated to be about 40 nm. The surface areas of the acid and base catalyzed gels were between 890-960 m^2/g, and the calculated particle size was between 2.9 - 3.1 nm for both CO_2 and high temperature SCD. Studies of light scattering during gelation indicated distinct differenced between acid and base catalyzed gels.

Schuck et al (57) studied the pore-size distribution on aerogel samples using BET gas adsorption-desorption with N_2 at 77 K and SAXS. From BET data for 3 samples of densities 275, 145 and 105 g/L, the specific pore volumes were 3.16, 6.42 and 9.05 cm^3/g respectively. For these aerogels, the largest pore-volume fraction (up to 90% for low-density samples) was found to be above the 60 nm diameter range, whereas from Rayleigh scattering an upper value of pore-size dimension of 200 nm was estimated. SAXS data indicated the most frequent particle diameter to be in the range of 5 - 6 nm (Fig. 7).

The microstructure of silica based aerogel was studied by Lampert et al (58), using high resolution electron microscopy. The samples were acid-catalysed TEOS aerogel dried by SCD at 270°C and 12 MPa. The chemical analysis of the samples was done with Scanning Auger Microscope and ESCA. The studies revealed that silica aerogel consists of a network of amorphous stoichiometric silica clusters with an average size of about 10 nm. The aerogel transformed readily under an intense electron beam - the sizes of the particles increased to 20-50 nm and appeared to be stable with time after the transformation. The structure of the transformed cluster was amorphous as determined by HREM.

Broecker et al (59) studied the structure of silica aerogel pellets at BASF. Pellets having apparent densities ranging from 0.133 - 0.287 g/mL were studied by mercury porosimetry and BET N_2 adsorption studies. (Table 3).

Gronauer et al (60) investigated mechanical and acoustic properties of silica aerogel. Longitudinal sound velocity varied between 100 - 300 m/s for aerogels of densities between 70 - 300 g/L. Compared to silica glass, an aerogel has an extremely small Young's modulus 10^6-10^7 N/m^2, and therefore can be compressed very easily. Aerogels which consist of primary SiO_2 particles a few nm in diameter that are interconnected by tiny necks 1 nm in diameter, have a mechanically soft and elastic structure, and thus have potential as a new acoustic material. Potential applications of aerogels include sound isolation at high temperatures, in acoustic delay lines, and use as an acoustic anti reflecting x/4-layer in piezoactive material.

Infra-red absorption studies on alkoxide gels showed the effect of added fluoride on Si-OH formation (61). The alcogel structure (after

complete water exchange) was characterized by thermoporometry and shown to consist of lightly connected cylindrical pores of 2.5 nm pore radii. (62). The shear modulus of silica gels was shown to be dependent on the concentration of silica in the alcogel (63).

The hydrolysis of TEOS to gel formation was followed by ^{1}H NMR (64). The signal of residual CH_2 and CH_3 in the gel dried for 4 months was present even when the mole ratio of H_2O/TEOS was 6. These organic groups disappeared when the ratio was increased to 15.

Sindorf et al (65) used solid state ^{29}Si NMR experiments, employing cross polarization (CP) and magic angle spinning (MAS) techniques, on a series of heat treated silica gels which were silylated by hexamethyldisilizane (HMDS). This was an attempt to elucidate details of the surface -OH population of unsilylated samples. They observed that the complete removal of all silanol groups from silica is probably approached only at temperatures higher than 1000°C. Their studies showed that ^{29}Si NMR methods can be used to measure surface -OH concentrations or bulk OH densities with good precision and accuracy, for silica gel samples that are preheated over a wide range of temperatures. Measurements are not complicated by the presence of molecular water, and therefore do not require the preparation of completely anhydrous samples. Further NMR studies favoured the linear growth model for gel formation (66) compared to the cyclic oligomers.

Vacuum and air dried gels studied by ESR after -radiation (67,68) and x-ray exposure (69), revealed that low temperature annealed gels showed the presence of organic free radicals, e.g. CH_3, and C_2H_5, whereas after high temperature annealing only the O_2^- radicals were detected. NMR and Raman spectroscopy was used to study the sol-gel

process for TMOS. The addition of formamide hinders the hydrolysis, in part by increasing the viscosity of the solution and thereby increasing the proportion of bulky dimers, which are slower to hydrolyse. Also, the strong hydrogen bonding of formamide with Si-OH and CH_3OH bonds tends to slow hydrolysis (70). The use of drying control chemical additives (DCCA) to affect gels in the formation stage and drying stage was reviewed (71). It was shown that formamide decreases the hydrolysis rate six-fold but increases the polymerization rate slightly.

Yoldas studied the hydrolytic and condensation process of TEOS (72,73) using NMR and size exclusion chromatography (SEC). In general it was concluded that higher concentrations of SiO_2 result in a higher number of bridging oxygens, (higher degree of polymerization). The hydrolysis of TEOS was compared with $CH_3Si(OC_2H_5)_3$, (MTES), and $(CH_3)_2Si(OC_2H_5)_2$, (DMDES), (74). Gel formation did not occur with DMDES where phase separation was noted. Viscosity and IR measurements showed TEOS and MTES to be similar in hydrolysis and polymerization.

Light scattering of silica sols was shown to validate the application of SEC (75). The gel formation from various alkoxides was studied, and air drying compared at room temperature and elevated temperatures (76). The various stages of the sol-gel process was followed by viscosity, IR, TGA, DTA, and BET measurements (77).

As indicated earlier the implication of aerogels for super insulated windows is a recent development (2). However, the subject has been patented in France by Zarzycki et al. (78). Thus, it would appear that besides the Berkeley group and the Swedish group there is a French group also involved in insulated windows. The results from the Berkeley group were recently reviewed by Hunt (79,80).

There does not seem to be any report on or attempt to freeze dry the alcogel. The drying of cellulose gels has been studied extensively, (81) and an apparatus is described by which the water can be continuously removed from a sample and replaced by ethanol. Freeze-dried cellulose acetate (82) was characterized by a porous structure that is useful for the separation of gases. There does not appear to be anything intrinsically wrong with the idea of freeze-drying the alcogel and this belief has been confirmed (83). A properly cross-linked transparent alcogel which is thoroughly exchanged with a high melting point solvent should dry at ambient temperature and pressure without cracking or becoming opaque. This has yet to be verified. Such experiments are in progress in the author's laboratory and results have been encouraging - transparent aerogels with porosity of about 70% have so far been produced.

V. Applications

A. High Energy Physics

The need for a low density material with good optical quality for use in Cerenkov counters played a historical role in the development of high quality, transparent aerogel. Cerenkov counters require a material with an index of refraction between 1.00 - 1.3. Detectors were previously made with pressurized gas, and required solid walls and heavy construction. Aerogel detectors can be easily constructed with an index of refraction between 1.007 - 1.24, are extremely light, and of simpler construction. Aerogel Cerenkov detectors (84,85) have been in use since the early seventies in accelerators at CERN, Berkeley and were recently in space astrophysics by NASA (86).

B. (i) Superinsulation - Thermal properties and Energy Conservation.

Because of their extremely low thermal conductivities, low densities and high porosity, an ideal application of aerogels is as a superinsulating window spacer with an extremely low loss coefficient of about 0.5 $Wm^{-2}K^{-1}$. In his pioneering work, Kistler demonstrated that the thermal conductivity of aerogel cakes is of the order of 0.02 $Wm^{-1}K^{-1}$ at ambient pressure in air, and 0.01 $Wm^{-1}K^{-1}$ if evacuated. Considering the high transparencies obtainable with aerogel, it is apparent that it has a vast potential for the reduction of heat losses in all kinds of window systems.

The first direct application of silica aerogels for transparent insulated windows was recorded by Schmitt and Greiger-Block (87). Schmitt used ethylorthosilicate instead of methylorthosilicate because of the higher toxicity of the methyl ester. Hydrolysis was performed with either hydrofluoric or hydrochloric acid. Because of the difficulty in handling large pieces of aerogel, the hydrolysis and setting of the alcogel was made directly between two plates of glass. Samples with porosities of 0.93 to 0.97 were recorded, with optical properties shown in Fig. 8(4). The results of some thermal conductivity measurements are given in Table 4a, b and c. Previously determined literature values are shown in Table 5a and b. The values which have been used (2) are about 0.02 $Wm^{-1}K^{-1}$. This can be reduced to half by the use of other filling vapours such as CCl_2F_2 (88,89,90).

Infrared heat transfer in transparent aerogel was investigated by Caps and Fricke (91). They have reported values for radiative conductivity of an evacuated double pane window with a silica aerogel spacer to be below 0.002 $Wm^{-1}K^{-1}$. They estimated the total thermal conductivity of aerogel to be in the order of 0.007 $Wm^{-1}K^{-1}$, which

corresponds to a total loss coefficient, U, of 0.7 $Wm^{-2}K^{-1}$ for a 1 cm thick aerogel tile. Thermal and solar optical properties of silica aerogel for use in super-insulating windows have also been investigated by Hartmann et al (92) at Berkeley. They report that radiation heat transfer through aerogel is not a significant problem in the temperature range relevant to insulating windows. Aerogel's thermal performance can be improved by replacing the pore gas with one of lower conductivity or by evacuating the aerogel to pressures below 0.1 atm. For a gap spacing of 12.5 mm, evacuated aerogel windows have a calculated U value of about 0.5 $Wm^{-2}K^{-1}$.

Goetzberger et al (93) reported that using aerogel as insulation for passive solar energy applications in buildings resulted in as much as 50% and 90% reductions, respectively for heat energy demand in three winter months in Freiburg . Another positive aspect of aerogel insulation is that it is non-flammable. Indirectly, as a result of the energy saving from aerogel insulation, adverse environmental consequences of present heating technology used in buildings would also be reduced.

Fricke et al (94) investigated the thermal loss coefficients of monolithic and granular aerogels used as superinsulating spacers under evacuation, and reported these to be around 0.5 $Wm^{-2}K^{-1}$ for layers about 15 mm thick. Variation of parameters such as radiative temperature, sample density, boundary emissivity and internal gas pressures were considered. Applications and benefits of thermal superinsulation with aerogel include i) systems such as hot water storage, ii) electric house heating/storage systems could be made smaller due to smaller losses iii) superinsulated steam heating systems and steam pipes with smaller diameters than conventional ones, iv) new high temperature batteries,

such as sodium sulphide batteries for electric vehicles which depend on load-bearing superinsulations to keep the reactants liquid during parking periods, v) superinsulated refrigerators and freezers could be built with less cooling power and larger useful volume for a given outer geometry than conventional systems, vi) energy-efficient operation of green houses, vii) solar ponds for collection and long-term storage of solar energy.

Nilsson et al (95) investigated the thermal conductivity λ, and the specific heat capacity ρc_p of aerogel as a function of temperature. They also considered the volume dependence of thermal conductivity, from the view point of window insulation using blocks of aerogel of dimensions as large as 190 x 190 x 32 mm. Thermal conductivity at atmospheric pressure and normal outdoor temperatures (-20° to $50^{\circ}C$) for two samples with initial density of 109 g/L were determined. Thermal conductivity at room temperature was found to be 0.0131 $W\ m^{-1}K^{-1}$, and increased linearly with T up to $40^{\circ}C$ where there was a sudden change of slope. At a temperature of $50^{\circ}C$, λ reached a value of 0.0178 $Wm^{-1}K^{-1}$. As the temperature was lowered, λ decreased with a slope of only 35×10^{-6} $Wm^{-1}K^{-2}$, giving a great hysterisis to the λ-T curve; however, there was no hysterisis effect noticed when cooled down to $-20^{\circ}C$ and then going back to room temperature - the value of λ after this cycle in temperature was 0.0167 $Wm^{-1}K^{-1}$. The second sample, taken up to $100^{\circ}C$ and then back to room temperature, showed similar behavior. The variation of heat capacity per unit volume, ρc_p, with temperature was also studied, and the quoted value at room temperature was 0.24 $MJm^{-3}K^{-1}$ with a corresponding c_p value of 2.2 $J\ g^{-1}\ K^{-1}$. A variation of 25% per $^{\circ}C$ was reported for c_p. Comparison with compressed material (up

to 0.4 GPa) revealed no pronounced difference in the c_p *vs* T curves, except that at the highest temperature (200°C) the uncompressed material showed up to 5% higher values for c_p. Variation of and c_p with pressure showed no marked changes in either quantities up to 25 MPa. A marked change occurred at that pressure; the change was time dependent, indicating that it may be due to volume relaxation.

Platzer et al (96) investigated the solar transmission of aerogel pellets of 0.5-8.00 mm diameter, produced by BASF Ludwigshafen, which were used as fillers in windows under different outdoor conditions. Because of the scattering of blue light, the outdoor transmittance varied depending on weather conditions. Transmittance values ranging from 64-70%, for 1 cm of filling thickness, were reported. A simple theoretical model was developed to calculate mean solar transmittance for aerogel layers, including a correction factor for scattering and absorption.

Schreiber et al (97) reported on the potential of aerogel as a transparent insulation material for buildings from an engineering viewpoint. Comparison of various insulating materials used in buildings were made, with reference to Copenhagen weather conditions and different wall constructions; the U-values for light-weight wall constructions were 0.27 $Wm^{-2}K^{-1}$ (insulated) and 0.81 $Wm^{-2}K^{-1}$ (uninsulated). Based on a model calculation, it was reported that an estimated 350 kwh/m^2 of heating energy could be saved per year, by insulating high-mass wall constructions with aerogel whereas for a light-weight type of wall, a saving of 50 kwh/m^2 per year would still be possible. Considering the given boundary conditions, the comparison of an equivalent opaque insulation to transparent insulation would yield a yearly specific

energy conservation of 30-100 kwh/m^2 for the transparent insulation, depending on the orientation and type of the wall material.

(ii) Aerogels in Luminescent Solar Concentrators (LSC).

Another important use of aerogels is in luminescent solar concentrators (LSC). A luminescent solar concentrator is a planar layer of materials, usually contained on or in a transparent matrix of plastic (98). The matrix is usually doped with an organic dye that fluoresces under incident solar radiation. If the refractive index of the matrix is sufficiently dissimilar from that of air, the fluorescent radiation is reflected and confined within the matrix, and is ultimately directed to the outer edges of the plane where solar cells for energy conversion are placed. This subject has been reviewed by Reisfeld and Jorgensen (99,100). Aerogel can be used as a material for flat bed solar concentrators when it is suitably doped with either organic or inorganic luminescent material, such as dyes or rare earth salts, and made continuous by filling the doped aerogel with a monomer such as methyl-methacrylate. Folcher et al (101) have described LSC containing uranyl doped glass, and obtained quantum yields of 0.6-0.7 with low uranyl concentration (<1%). Avnir et al (102) reported their work on Rhodamine 6G embedded in porous silica gel glass prepared from TMOS, and discussed the advantages of inorganic oxide glasses as carriers of organic dyes. These advantages included photo and thermal stability of the glass matrix, trapping of the dye molecule and its total isolation from undesired interaction with the neighboring dye molecules, impurities and photo decomposition products; non-leachability

of the dye, the ability to reach stable, yet very high dye concentrations, reduction of translational, rotational and vibrational degrees of freedom of the trapped dye and good transparency down to the U.V. region. Reisfeld (100), in another review, discussed the fluorescence and non-radiative relaxations of rare-earths in amorphous, and on highly porous materials such as porous Vycor glass, as well as applications of rare earths Nd^{3+} and Ho^{3+} in combination with UO_2^{2+} in luminescent solar concentrators.

C. Sol-Gel Route to Glass Manufacture

Aerogels have also been used as a means of preparing low temperature glasses. Such work generally consists of incorporating various different metal oxides within the gel to give rise to blends of silica glass (103-107). A recent review of this topic was presented by Mukherjee (108). It is interesting to note that the conversion of the gel to glass does not involve the removal of solvent by an autoclave at supercritical conditions. Numerous examples of such low temperature glasses have been described (109-116). The papers of a symposium, "Glasses and Glass Ceramics from Gels" in July 1983, have been published (117-143).

Since the purpose of all of these papers was to prepare a low temperature glass, the object of the process was to obtain a gel of high density. Gels of low density (0.60 g/mL) were reported (122) when drying was slow, but no mention is made of the transparency of the aerogels formed.

Though most of the symposium papers presented methods to prepare a pure or mixed gel, the control of viscosity was used (126) to reproduce pour conditions. Shrinkage was found to be greater when drying was conducted at higher temperatures (127). Yoldas (129) discussed the factors affecting gel formation and structure, the important ones being the selection of starting compounds and host medium, water/alkoxide ratio, molecular separation by dilution, catalytic effects, reaction temperature, order of reactions in multi component systems, aging and heat treatment which involves time, temperature and atmosphere. The influence of these factors were discussed with respect to gel formation involving $Si(OC_2H_5)_4$, $B(OCH_3)_3$ and $Al(OC_4H_9)_3$.

Congshen et al. (126) discussed the formation of ZrO_2-TiO_2-SiO_2 glasses by the sol-gel method. These glasses have low thermal expansion and are resistant to alkali corrosion, but it is difficult to prepare them by the conventional melting method because of their extraordinarily high melting temperatures (ZrO_2: $\sim 2700^oC$, TiO_2: $\sim 1850^oC$, SiO_2: 1713^oC). They synthesized these glasses by the sol-gel route using $Zr(NO_3)_4.5H_2O$, $Si(OC_2H_5)_4$ and $Ti(C_4H_9)_4$ and the resultant glasses contained 20 mol % TiO_2 and up to 30 mol % ZrO_2. Their detailed studies of hydrolysis, polymerization, gelation and conversion of gel to glass made use of I.R. spectroscopy, DTA and XRD. Viscosity evolution of the reaction system showed that environmental humidity and the catalyst used were important factors in the gelling process. During heat treatment, the colour of the gel changed gradually, and DTA results indicated that the conversion of gel to glass would be complete at 650^oC. From XRD and IR data they concluded that Ti^{4+} act as network formers, while Zr^{4+} act

as network modifiers. The formation of gels from coloidal SiO_2 particles were also reported (130)(131)(133). Gels prepared for spinning fibers have been described (135). In most cases, densification of the gel is encouraged, since the end use is a solid glass (136). Thin coatings and plates (137) invariably broke into fragments on drying. The short review by Dislich (138) clearly illustrates the scope of the sol-gel technique. The remaining symposium papers (139-143) discuss special applications of the process.

Schlichting (132) discussed oxygen transport through glass layers formed by a gel process. Oxygen diffusion rates for binary B_2O_3/SiO_2, GeO_2/SiO_2, Al_2O_3/SiO_2 and TiO_2/SiO_2 glasses were determined. To this end, silicon single crystal material was coated with the appropriate glasses obtained from gel solutions by a dipping process, and was subsequently heat treated. Schlichting pointed out that while it was difficult to prepare two component glasses by a melting process, it is easy to prepare thin glass films of every composition, mostly on glass plates, by a gel process.

Segal (133) made a comparative study of two sol-gel routes used to oxide ceramics, the first using colloidal dispersions and the second using metal alkoxide precursors. Methods of making shaped products such as spheres were described, with the range of oxides that have been produced using sol-gel routes. The sol-gel route involving metal alkoxide is ideally suited for the preparation of small quantities of high-purity materials. The sol-gel processes which employ dispersible oxides can be used for large scale production since they offer advantages for materials and energy economy.

Pentinghaus (134) discussed the use of alkoxide derived gels as starting materials in experimental petrology and solid state chemistry. Amorphous and homogeneous solids of many compositions can be prepared from alkoxide solutions via complexing, hydrolysis and polycondensation followed by a final heat treatment. Many alkoxides of Na, K, Cs, Si, Ge, Be, and Al were used in his studies.

Jones et al (135) described their studies on the use of technical ethyl silicate for preparing glass like materials and fibers. Technical grade ethyl silicate was hydrolysed using tetravalent organotin compounds as catalysts for neutral hydrolysis and gelation. Transparent, glass-like gels can be formed, particularly if the water content is greater than 16%. Systems with a water content between 8 - 16% show good fiber forming ability, dibutyl tin diacetate being the preferred catalyst. These systems show better fiber forming ability than do similar systems using tetraethoxysilane. Viscosity measurements suggest that this is because the technical ethylsilicate contains a mixture of linear polysilicate oligomers.

Glaser et al (136) discussed their work on the effect of the variation of H_2O/TEOS ratio on the preparation and nitridation of silica sol-gel films. These films have many potential applications, particularly as scratch resistant coatings, dielectric films, and oxidation or diffusion barriers. The film properties can be greatly enhanced by incorporation of nitrogen. Nitridation reactions provide a means for probing the surface chemistry and micromorphology of sol-gel films. Silica sol-gel films were deposited on silicon wafers by spinning solutions of varying H_2O/TEOS ratio. The density of initial microporous dried gel films increased with the H_2O/TEOS ratio, and the

amount of film shrinkage observed during thermal treatment in N_2 or NH_3 was decreased with increasing H_2O/TEOS ratio. This is contrary to the behavior of bulk gels derived from solutions of increasing H_2O/TEOS ratio. The trend is attributed to the fact that in films polymerization of the structure occurs in the absence of a liquid phase. Enhanced incorporation of nitrogen was observed during ammonia treatment of the films prepared with solutions of increasing H_2O/TEOS ratio. Nitrided films showed signs of limiting the oxidation of the silicon wafers.

Sakka et al (137) discussed the formation of thin sheets and coating films from alkoxide solutions. Thin sheet formation is only possible with the starting solutions which exhibit spinnability in the course of hydrolysis and polymerization of the metal alkoxide. Thin sheet formation becomes possible when the solution reaches viscosities ranging from 10-100 P, and is possible from solutions with H_2O/TEOS = 1.5 - 4. The gel sheet becomes a transparent silica glass sheet, 10-40 μm thick, on heating to 800-1200°C. Three methods were employed for thin sheet formation - the first involved putting a wire ring into the solution and pulling it up so that the sheet formed on the ring, for the second method, the viscous alkoxide solution was drawn into sheets by passing through a slit, and in the third the viscous solution was applied onto a non-adhesive plastic plate and removed after solidification. Coating films were applied to the substrate by the dip-withdrawal method. The films were then heated to convert the gel film to glass or ceramics. SiO_2, $BaTiO_3$ and transition metal oxide - SiO_2 coating films were prepared, and transmittance characteristics were reported.

Dislich (138) reviewed the scope of the sol-gel processes and pointed out that for economical reasons, the sol-gel products must have special uses or process advantages. He noted the most interesting fields to be preforms for communication fibres, technical fibres drawn from solutions, unsupported films, hollow spheres for nuclear fuels, catalytic effects, and coatings. Coatings are the oldest sol-gel products which have gained new impetus from multi component oxide syntheses. In this field, heat mirror coatings such as indium-tin-oxide (ITO) on float glass, necessary for energy saving windows, are of greatest interest. Ideal requirements for products and processes involved in the development of coatings were discussed.

Arfsten (139) discussed applications of sol-gel derived transparent IR reflecting ITO semiconductor coatings. ITO film reflects long wave IR radiation and thereby suppresses heat transport by radiation exchange. These films are highly transparent for solar radiation and therefore windows composed of ITO coated glasses are good passive solar collectors. A dip coating process for sol-gel derived ITO layers was developed and the characteristics of such ITO coatings were described. Transmittance as high as 83% in the visible region, radiant transmittance of 66%, and total energy transmittance of 74% were reported.

Geotti-Bianchini et al (140) described the preparation and characterization of Fe, Cr and Co oxide films on flat glass from gels. One component and multi component coatings were obtained on soda lime glass, their oxide content was determined and their transmittance and reflectance were measured in the 300-2300 nm range. The sun-shielding performance of these coatings were less than commercial sun-shielding glass.

Kaiser and Schmidt (141) reported that siliceous membranes can be reacted onto the surface of porous supports using the sol-gel method. Of the various possible techniques, reaction via the vapour phase is the most useful. A belt of filter media could be coated continuously and homogeneously using laboratory scale equipment; the coated filter media showed improved cleaning behavior compared to uncoated samples.

Carturan (142) discussed the preparation of supports for catalysis by the sol-gel route. The surface area and thermal stability of $SiO_2/Al_2O_3/Na_2O$ supports prepared from alkoxides were studied as a function of time and temperature. The results indicated substantial stability in time at temperatures $\lesssim 250^{o}C$, while progressive decrease in porosity was observed at higher temperatures. New supports were prepared by coating glass microspheres with layers of porous oxides such as Al_2O_3, TiO_2, ZrO_2, MgO, SiO_2, Fe_2O_3. Formation of the porous layer was achieved by extending the gel method to the coating technique. BET surface area, electron microscopy results, and other features relevant to these systems were discussed. The data suggests that these materials may be exploited as effective supports for metallic catalysts.

Philip and Schmidt (143) discussed methods of synthesizing materials for hard contact lenses from an epoxide substituted Si and Ti alkoxide, using the sol-gel process. To obtain sufficient tensile strength, polymethacrylates were incorporated as linear crosslinking elements, using a methacryloxy substituted alkoxysilane as a hook between the siliceous network and the polymer chain. The incorporation of titania led to dense monolithic products which could be cured with only minor shrinkages. Good wettabilities (contact angle with water

$(25\pm5)^{\circ}$ are due to glycol groupings formed by the epoxide radicals. O_2-permeabilities of $P = (13\pm1) \times 10^{-11}$ ml O_2 cm^2 ml^{-1} s^{-1} mm Hg^{-1} result from the silicone-like -O-Si-R structure elements, where R denotes a silicon-carbon bound organofunctional radical. The corresponding values for silicone rubber, another material used for contact lenses, are - contact angle with water: $85\text{-}100^{\circ}$, $P = 70 \times 10^{-11}$ ml O_2 cm^2 ml^{-1} s^{-1} mm Hg^{-1}. Though silicone rubber has a very good oxygen permeability, it is very hydrophobic. Thus the Si and Ti glasses prepared by the sol-gel process have an advantage.

Mulder et al. (144) discussed the preparation, densification and characterization of autoclave dried silica gels. A two step hydrolysis process was followed - first, tetraethoxysilane (TEOS) dissolved in ethanol was partly hydrolyzed at $50^{\circ}C$ with acidified water. Then polymerization was achieved by adding alkaline water at room temperature; the gelling time is dependent on the proportion of acid and base solutions added and can be reduced to a few minutes by the addition of the alkaline solutions. Before gelling, the solution was poured into molds of desired shape. The molds were coated with a two component silicon rubber which saves as an antiadhesive layer. The gel was dried in an autoclave in the presence of an inert gas (N_2) and at supercritical conditions ($300^{\circ}C$, 8 MPa). By using extremely dilute solutions, extremely low density gels were obtained. Very low densities of 0.03 g/mL and a specific surface area as high as 1600 m^2/g were achieved (Table 6a-c). TEM studies characterized the structure of the gels as a highly branched network of SiO_2 spheroids of diameter less than 20 nm. A TEM study of the densification of low density gels to glass revealed that during heating, spherical particles of porous

material coalesce into larger spherical particles of SiO_2, while the interconnected structure of the gel remained unbroken. The structure began to show serious alterations only after 800°C. At 1250°C the densification was almost complete in 12 minutes as a consequence of polymerization by the continued dehydration.

Achtsnit (145) described the development of microporous silica fibers from sodium silicate. By chemical and physical modification of a commercial product, a spinnable high viscosity dough was obtained. Sodium silicate fibers are the intermediate product; as a result of a cation exchange, the hydrolysis sensitive fibers were converted into silica fibers in an acid bath, and subsequent washing with water yielded a silicon dioxide content above 99.6%. The physical properties, particularly porosity and tensile strength, can be influenced in the final drying process. These low density fibers (1.5 - 2 g/mL) are the lightest inorganic fibers available and they have a low thermal expansion coefficient, good thermal stability up to 1100°C, and a low dielectric constant (4 at 1 MHz). Because of their low thermal conductivity, they could also be used in thermo-electric insulation sectors.

Pettit and Brinker (146) discussed the use of the sol-gel method for producing thin films for solar energy applications. Thin films were formed by depositing the alcohol/water solution of alkoxides of Si, B or Al on a substrate by spinning, dipping or spraying. On heating the film to moderate temperatures, 400-500°C, dense glass films or stable porous films were produced. The main aspects of solar energy applications discussed were: (i) encapsulation of black chrome solar selective coatings improved the high temperature thermal stability by a factor of 2.7; (ii) formation of porous, antireflective coatings on glass

envelopes used in solar thermal collectors increased the solar transmittance of the glass from 0.91 to greater than 0.96; (iii) double-layer, antireflective coatings of SiO_2-TiO_2 on silicon solar cells reduced their solar reflectance from 0.36 to 0.04, and thereby improved cell efficiencies by about 50%; (iv) protective coatings applied to silvered stainless steel substrates were used to form structural solar mirrors. Averaged solar specular reflectance values of 0.90-0.91 were obtained.

Avnir (147) et al utilized the sol-gel process to incorporate several organic dyes including Rhodamine 6G in inorganic oxide thin films. Fluorescent thin films were prepared by this low temperature sol-gel process with the aid of a surface active agent with good homogeneity and reproducibility. A variety of fluorescent molecules were embedded either in silica or silica-titania films. The dye molecules were not leached out by water. Absorption and emission spectra, enhanced photostability, longer life times and energy transfers between trapped dye molecules were described and discussed in terms of the effects of molecule matrix-isolation on these properties.

Gel formation in alumina and silica from the alkoxides has been studied by Yoldas (148). The Raman and IR changed in a gel when heated from 40° to 500°C, and was used to follow the process of glass formation in TEOS to SiO_2 (149).

Mixed oxide gels of TiO_2-SiO_2 were prepared by Yamane et al. (150) by using a bulky alkoxide for $Ti(OR)_4$ and a methoxide for $Si(OR)_4$. Several methods were compared, but the work only considered the homogeneity of the glass. A similar study was reported by Gonzalez-Oliver (152). The gels were dried first at room temperature,

and then in a ventilated oven at 50-60°C for 3 to 4 weeks. The gels obtained were hard, clear and crack-free. However, no density values were given. Similar mixed glasses of SiO_2-TiO_2 were prepared by Hayashi et al. (152) by the alkoxide-gel process. The drying process for the gels took 3 months. Though transparent glass was formed at 800°C no mention was made of the properties of the gel. Some recent work reported (153) on silica-alumina gels which have been made from the silicon alkoxide hydrolyzed with $Al(NO_3)_3$ in alcohol. However, the gels were ground to a powder before being fired at high temperature. A gel from $NaOCH_3$ and $B(OBu)_3$ was reported to fuse at 500° to full densification, and to resemble the melt quenched glass (154). Drying of the gel took several days as the temperature was raised from 25° to 500°C.

An interesting review of the applications of sol-gel glasses has been given by Dislich (155). Though numerous applications are described, the insulating properties of the aerogel were omitted.

Gel formation starting with pyrogenic silica was described in terms of the characteristics of the starting silica (156). DTA and NMR were used to determine the extent of bound water. Ultrasonication of the aqueous dispersions tended to break up the clusters (157). The polymerization of siloxanes was reviewed (158) in relation to glass formation.

The structure of gels in relation to glass formation was described by Zarzycki (101). Comparison was made between the open pore and closed pore models.

Raman studies were reported on TiO_2/SiO_2 glasses prepared by the sol-gel process (160).

Wenzel (161,162) has summarized the role of the sol-gel process and its effect on the glass industry.

Gel formation from fumed silica in various organic solvents were studied primarily by TGA (163). Several papers by Brinker and Scherer on the sol-gel-glass process have presented a good review of the process and its problems (164-167). Potential application of the sol-gel process was detailed by Gottardi (168).

Coloured coatings were prepared by the sol-gel process by adding Co, Cr, Mn, Fe, and Cu to the gelling solution. Thin coatings of the gel were not coloured sufficiently to have suitable applications (169).

Gonzalez-Oliver et al (170) described electroactive antimony-doped tin oxide coatings on display and borosilicate glasses. They were prepared by dip-coating and spraying techniques, starting from alkoxides in n-butanol or acetylacetone solvents containing small quantities of catalysts and water.

Electron micrographs of silica xerogels showed particle agglomeration during heating to form dense glass (171). The effect of fluoride on gel formation and drying was studied, adn it was determined that shrinkage decreases with the addition of fluoride (172). Gels dried in an autoclave at super-critical conditions were shown to exhibit no shrinkage when the initial N_2 pressure in the autoclave was about 80 atm (173).

A series of papers by Scherer on gel formation and drying (174-179) have clearly defined the problem and present some interesting solutions. The gel to glass process was reviewed by Dislich (180). Other aspects of glass prepared by the sol-gel process have been outlined (181-187).

Krol et al (188) used Raman spectroscopy to study the influence of gelling in an autoclave and drying with $SOCl_2$ or Cl_2 on the properties of monolithic silica gels, with emphasis on the surface and bulk OH content and densification behavior.

Suwa et al (189) described the densification and sintering behaviour of structurally diphasic Al_2O_3 and Al_2O_3-MgO xerogels. With isostructural seeding, they were able to achieve enhanced densification as well as sintering at lower temperatures. Microstructural characterization by XRD showed uniform grain growth with little or no porosity.

Oda et al (190) applied the sol-gel method to prepare ultrafine α-$LiFe_5O_8$ particles using alkoxide as the starting material.

Sun et al (191) described the preparation of rare-earth silicate glasses by the sol-gel method starting with rare-earth carbonates of Pr, Dy, and Er and TEOS, and densifying the gel at 800°C. Infra red and visible spectra and magnetic susceptibilities were reported.

Tanaka et al (192) studied the mechanical instability of gels at the phase transition - when immersed in a liquid, gels undergo a volume phase transition, with the volume change at the transition as large as a factor of a thousand. The physical basis underlying the formation and evolution of the pattern during swelling is discussed for an ionized acrylamide gel as an example. An ESR and ENDOR study of the V_2O_5 gels was reported by Barboux et al (193). They studied the swelling of the gel in water and showed that water molecules belong to the co-ordination polyhedron of V(IV) ions, giving rise to hydrated vanadyl species.

Bali et al (194) studied the conduction mechanism in V_2O_5 xerogel films of thicknesses ranging from 5 and 1000 nm, and showed that the

conduction is purely electronic. Conductivities are two orders of magnitude higher than those of single crystal V_2O_5 and two orders of magnitude lower than the V^{4+} concentration in either the films or the single crystals. Bali suggests that the higher conductivity of xerogels is associated with film hydration which increases the number of V^{4+} sites active in the conduction process.

Calenczuk et al (195) discussed specific heat and thermal conductivity measurements, performed in the temperature range 0.1-10 K, on low density silica aerogels (0.27-0.87 g/mL) and commented on the unusual behavior compared with glasses. The results, together with the sound velocities data, were interpreted within a fractal model of the structure.

The sol-gel process applied to the encapsulation of nuclear waste (196) was described. Plodenic (197) discussed the vitrification of nuclear waste, and the problems to tackle in relation to glass technology for containment of 50-60 radioactive elements in a durable borosilicate glass.

The sol-gel method was used to prepare TiO_2 film on nesa glass substrate. The sol was prepared by mixing $Ti(OiC_3H_7)_4$, anhydrous C_2H_5OH and water. The film was obtained by dipping a nesa glass substrate in the TiO_2 sol and subsequently pulling it up at constant speed (0.15 mm s^{-1}). The resulting film was heat treated at 500°C for 10 min. The above operation was repeated until a thick film of 2 μm was obtained. The dip-coating method makes it possible to obtain a large surface area of thin films, which might have great effects on the photoelectrochemical behavior of this semiconductor, which is used as a photoelectrode in solar energy conversion (198,199).

The importance of the sol-gel method in making nuclear fuel pellets, low-temperature ceramic material such as ceramic fibers, thin coatings and abrasive grain has been reviewed (200), with special emphasis on the increasing likelihood of developing electronic ceramic materials. Although purity and control of the stoichiometry of these ceramics is essential, thin layers are adequate. Recently the sol-gel process has also been applied to the preparation of high temperature ceramic superconductors, such as YBa_2CuO_{6+x} (T_c = 91 K) $La_{1.9}Ba_{0.1}CuO_4$(T_c = 23 K) (200b).

D. Other Applications

(i) Catalysis

Aerogels show great promise in catalytic applications. Teichner and co-workers detailed some recent applications of aerogels as catalysts. Compared to conventional catalysts, their activity and selectivity in various catalytic reactions appear to be much higher. Besides, in some catalytic reactions common catalysts become deactivated with time on stream.

Teichner (201) reported on the preparation of aerogels of inorganic oxides; pure as well as mixtures of two or more oxides. In the case of binary or ternary oxides, the less refractory ones such as NiO may be reduced to the metallic state, in which the metal particles are stabilized in the divided form by other oxide(s) like silica or alumina which act as support of the metal. Besides silica, other examples were Al_2O_3, ZrO_2, MgO, Fe_3O_4, TiO_2, Al_2O_3-MgO, TiO_2-MgO, ZrO_2-MgO. Mixed oxide aerogels that have good catalytic properties were cited as Al_2O_3-NiO, Al_2O_3-Cr_2O_3, SiO_2-NiO, SiO_2-Fe_3O_4. Some examples of aerogel catalysts are described below.

TiO_2 Aerogels

TiO_2, in the form of anatase, exhibits a surface area of 120 m^2/g and is used at room temperature as a photocatalyst for partial oxidation

of paraffins, olefins and alcohols into ketones and aldehydes. In the case of paraffin-like isobutane, the conversion yield is higher on the TiO_2 aerogel than on other forms of anatase.

Gels have been used for stabilization of reactive free radicals. Gesser et el (202) stabilized a high concentration O_2^- on the surface of amorphous TiO_2 gel, which was annealed at temperatures less than 550°C. Ragai (203) reported on the production of trapped O_2^- free radicals generated in a titania gel matrix by the initial reaction of Ti(III) ions with H_2O_2, and the subsequent precipitation with NH_4OH. The detected paramagnetic species could be complexed with Ti(IV) ions. The trapped O_2^- free radicals had a high stability extending as long as 2 years.

Fe_2O_3/SiO_2 and Fe_2O_3/Al_2O_3 Aerogels for Fischer-Tropsch Synthesis

These catalysts, which have surface areas of the order of 800 m^2/g, are important in view of their direct potential in alleviating the inevitable shortage of crude oil. Teichner et al (204a,b) reported that ferric oxide supported on silica or alumina aerogels shows a catalytic activity in the F.T. synthesis of hydrocarbons from catalytic hydrogenation of carbon monoxide, that is 2-3 orders of magnitude higher than that of the commonly used reduced iron catalyst.

Ni/Al_2O_3 Aerogels

These catalysts are obtained by hydrogen reduction of NiO/Al_2O_3 aerogels (204b). The good dispersion of nickel is preserved only when the stoichiometric amount of water is used in the hydrolysis of the starting organic derivatives. In the dealkylation of ethyl benzene into benzene, the aerogel catalysts show limited selectivity (1%) towards the undesirable side reaction of the rupture of the aromatic ring.

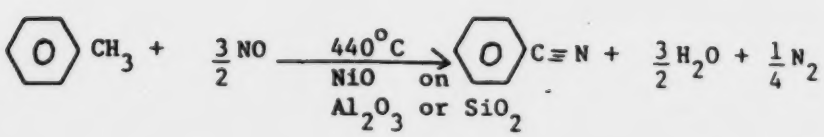
Cu/Al_2O_3 Aerogels

These aerogels have been used in a fluidized bed reactor for selective hydrogenation and cyclopentadiene into cyclopentene with a selectivity of 100% at a reaction temperature of 180-220°C (204b). They are also 100% selective towards the partial hydrogenation of acetylene to ethylene.

NiO/Al_2O_3 Aerogels

NiO/Al_2O_3 aerogels are almost 100% selective towards partial oxidation of olefins (204b). Isobutene is converted to methacroleine and acetone. NiO/Al_2O_3 aerogel is selective towards partial oxidation of n-propane (50%) and of isobutane(75%) to acetone. With ternary aerogels NiO/SiO_2/Al_2O_3 the selectivity may even be 100%.

Nitriles are intermediate monomers for the plastic polymers like polyacrylonitrile and polymetacrylonitrile. The usual method is based on the oxidation of olefins in the presence of oxygen and ammonia (ammoxidation) and of conventional catalysts containing oxides of Sn and Sb or of Mo and Bi. Paraffins and aromatics are not converted into nitriles by these catalysts. Teichner reported that by using NO in the presence of NiO/Al_2O_3 or Ni/SiO_2 aerogel at 440°C, toluene and xylenes could be converted into the corresponding nitriles, propene into acrylonitrile, and isobutene and isobutane into methacrylonitrile. In some cases selectivities as high as 90% were attained.



The aerogel catalysts were prepared from a solution of nickel acetate and aluminium sec-butoxide which were both dissolved in methanol and hydrolyzed by the stoichiometric amount of water to yield the mixed alcogel. This alcogel was finally evacuated in an autoclave in hypercritical conditions with respect to methanol. Cr_2O_3/Al_2O_3 aerogels equally effective (204b).

Xylenes were also converted into nitriles with a $PbO-Al_2O_3$ aerogel catalyst (204b). With orthoxylene, the selectivity in orthotolunitrile is 75% and 20% in phthalonitrile. With paraxylene the selectivity in dinitrile is 50% with the same catalyst at 460°C, using a feed containing an excess of NO (P_{NO} = 30 torrs, P_{xylene} = 15 torrs, P_{He} = 715 torrs)

<u>Pd/Al_2O_3 Aerogel</u>

Armor (205) et al reported the use of Pd/Al_2O_3 aerogel, which had large pore volumes (6.5 cm^3g^{-1}) and high surface areas (642 m^2g^{-1}), in complete and selective hydrogenation of nitrobenzene to aniline. Yields higher than 1000 m moles of aniline/m moles of Pd were observed. Because of their enormous pore volume, aerogels have further potential as catalysts in hydrodenitrogenation and hydrodesulfurization processes.

Wang et al (206) reported that some oxides directly produce ethyl acetate from ethanol. Acetaldehyde was formed by oxidative dehydrogenation, and reacted further with the remaining alcohol to produce the ester. Bi_2O_3, MoO_3 and Sb_2O_4 showed good activity for ethyl acetate formation. However, binary oxides $MoO_3-Sb_2O_4$ showed much higher activity. Increased activity and selectivity for ethyl acetate was attributed to the formation $Sb_4Mo_{10}O_{31}$ during the course of the reaction. It is probable that these oxides in the aerogel form could still be much more effective and selective.

Bond and Flamerz (207) discussed the structure and reactivity of titania supported oxides. Around 473 K, both titania (TiO_2) and Vanadia (V_2O_5) act principally as dehydration catalysts. VO_x/TiO_2 catalysts, prepared either by impregnation with NH_4VO_3-oxalic acid solutions or by grafting methods using $VOCl_3$ or $VO(OiBu)_3$, exhibit a faster rate of acetone formation than propene formation. Rates were found to be almost independent of V_2O_5 content in the one to ten monolayer range, and a one monolayer point was 50 times faster on a weight basis than with unsupported V_2O_5. Activation energies for both reactions - decomposition of isopropanol by a) dehydration to propene and b) by dehydrogenation to acetone, are markedly lower for the monolayer catalysts than for the TiO_2 supports, and selectivity to acetone increases with decreasing temperature. Activity is attributed to the vanadate groups in the monolayer, and a mechanism involving V=O and V-OH groups is proposed for the dehydrogenation reaction.

(ii) Aerogels for Gellifying Rocket Propellants

Because of the large pore volume of aerogels, a small weight of these solids may confine a large volume of liquid. Aerogels also appear to have the ability to develop viscosity and thixotropic behaviour in liquids, and hence their use as good thickening agents for water, gasoline, red fuming nitric acid (RFNA) and unsymmetrical dimethylhydrazine (UMDH), in fuel. In all cases, the gels obtained are thixotropic viscoplastics with fairly high shear stress (eg. 0.6 kPa) thresholds. The macropore volumes of aerogels govern their thickening capabilities. Teichner and co-workers (204b) were able to jellify more than 20g of RFNA and 40g UMDH per 1 g of silica aerogel. The gellifying

ability of aerogels is correlated with their macropore volume, and is independent of their surface area.

(iii) The Aerogel method is also used for carbon-carbon composite densification (204b). Carbon composites are macroporous materials which must be filled by carbon black using thermal cracking of methane at high temperatures (CVPD process). They are used for rocket nozzles, oxidation-resisting units, molten-salt reactors, heat exchangers etc. Standard CVPD conditions are 1000°C and 1 kPa of methane. The CVPD procees is time and energy consuming and does not lead to the maximum permissible density of the carbon composite. The same carbon composite can be impregnated by a solution of $Si(OCH_3)_4$ (TMOS) in methanol with the stoichiometric amount of water to yield a dense aerogel of 120 g/mL. This aerogel can then be evacuated in the autoclave under hypercritical conditions with respect to methanol, and the resulting composite containing silica aerogel is more easily amenable to densification by the CVPD process. In applying the silica aerogel method, one must ensure, however, minimum shrinkage and elimination of SiO_2. At 700°C dense silica aerogels exhibit only slight shrinkage. Silica is finally vaporized at 2500°C without damage of the carbon material.

(iv) Silica Aerogels as Insecticide

It has been claimed that silica aerogel is a more efficient killer of wood-termites than the well known insecticide DDT (201,208). Chemically inert dusts of very fine particle size and high surface area can kill insects in grain and seeds as well as other earthly anthropods such as mites, ticks, cockroaches, silver-fish, ants, fleas, and termites, by adsorbing and abrading their protective lipid layer. Mortality results from the rapid loss of body fluids from the

organic tissue. This physical, rather than chemical, activity of aerogels as an insecticide would be a safe and desirable attribute from an environmental point of view.

Other applications of aerogels can be found in gel permeability chromatography, oil recovery, storage and transportation of dangerous liquids.

VI Conclusion

Aerogels are extremely porous high-tech materials and show great promise in a variety of applications. The existence of a massive volume of literature concerned with the sol-gel process indicates the vast scope of the method. Widespread passive solar energy application of aerogels - primarily use as super insulation - would require cheaper methods of production, especially in relation to drying. In order to be economically viable, the use of autoclaves must be avoided. An alternative freeze drying method which employs solvents with higher melting points, developed in the author's laboratory, appears to be a promising approach.

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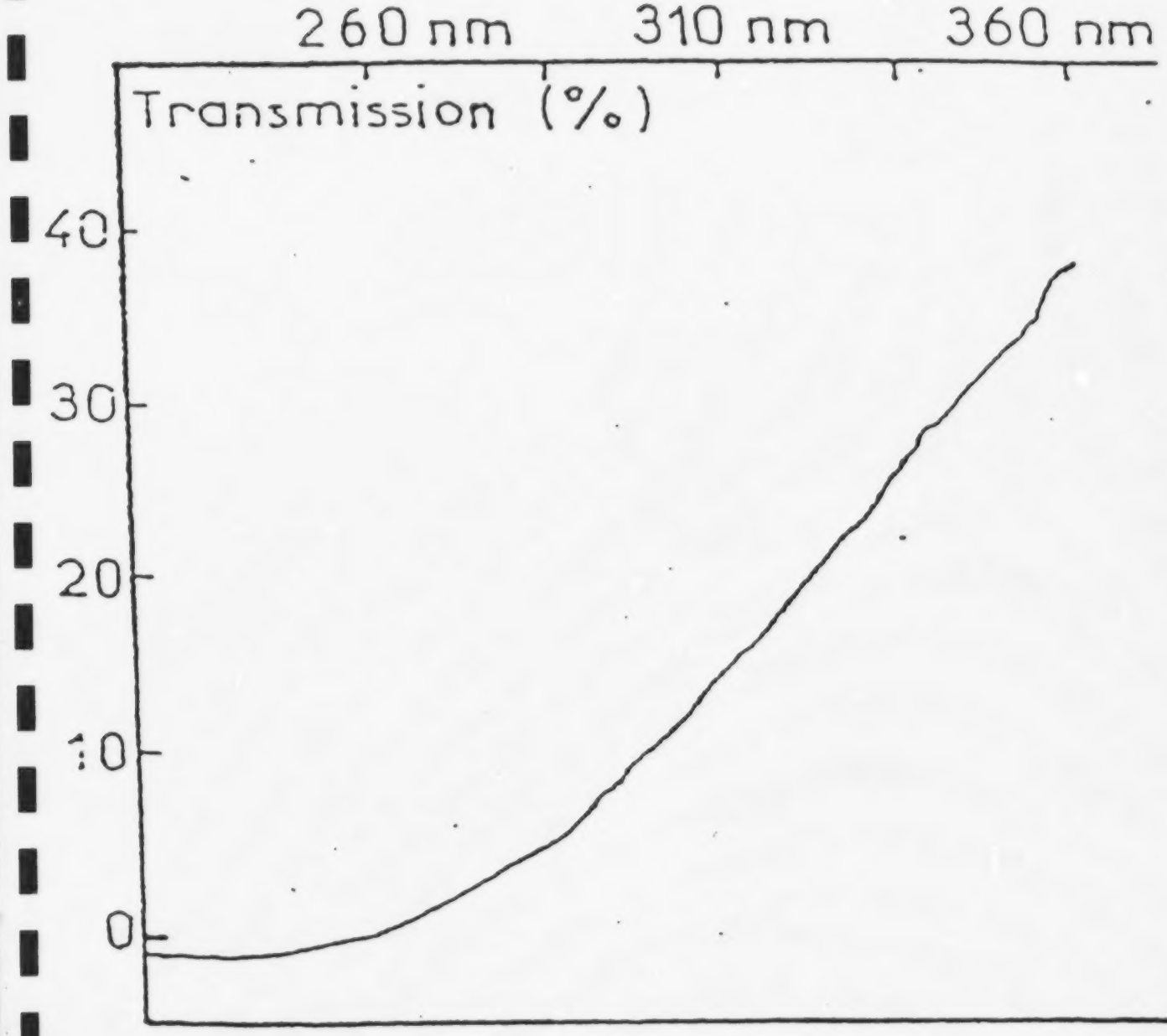


Fig. 1A - UV transmission of a silica aerogel (density 0.16 g/ml) of 0.4 mm thickness. (14)

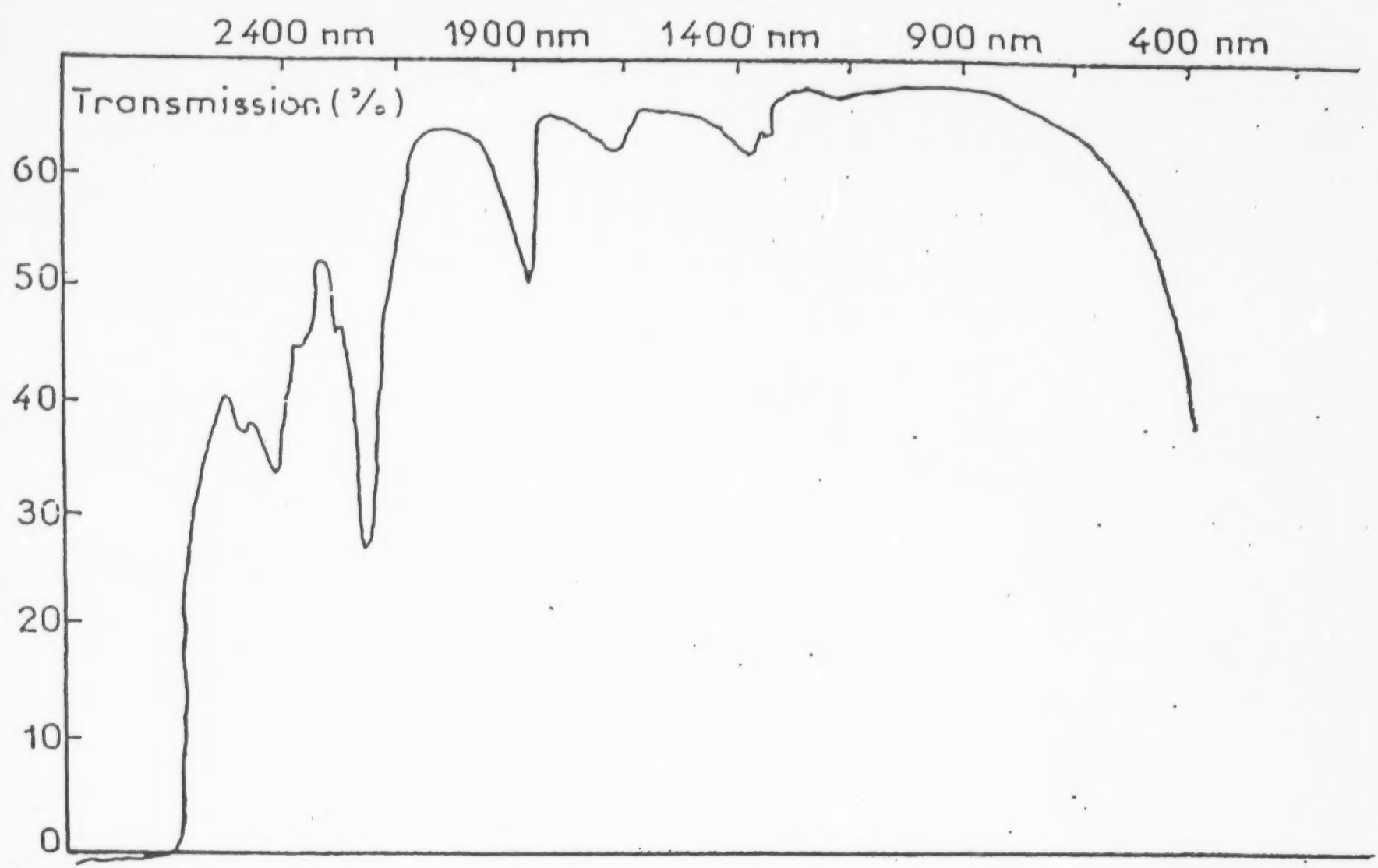


Fig. 1B - Visible and near IR transmission of a silica aerogel. (density 0.16 g/ml) of 0.4 mm thickness. (14)

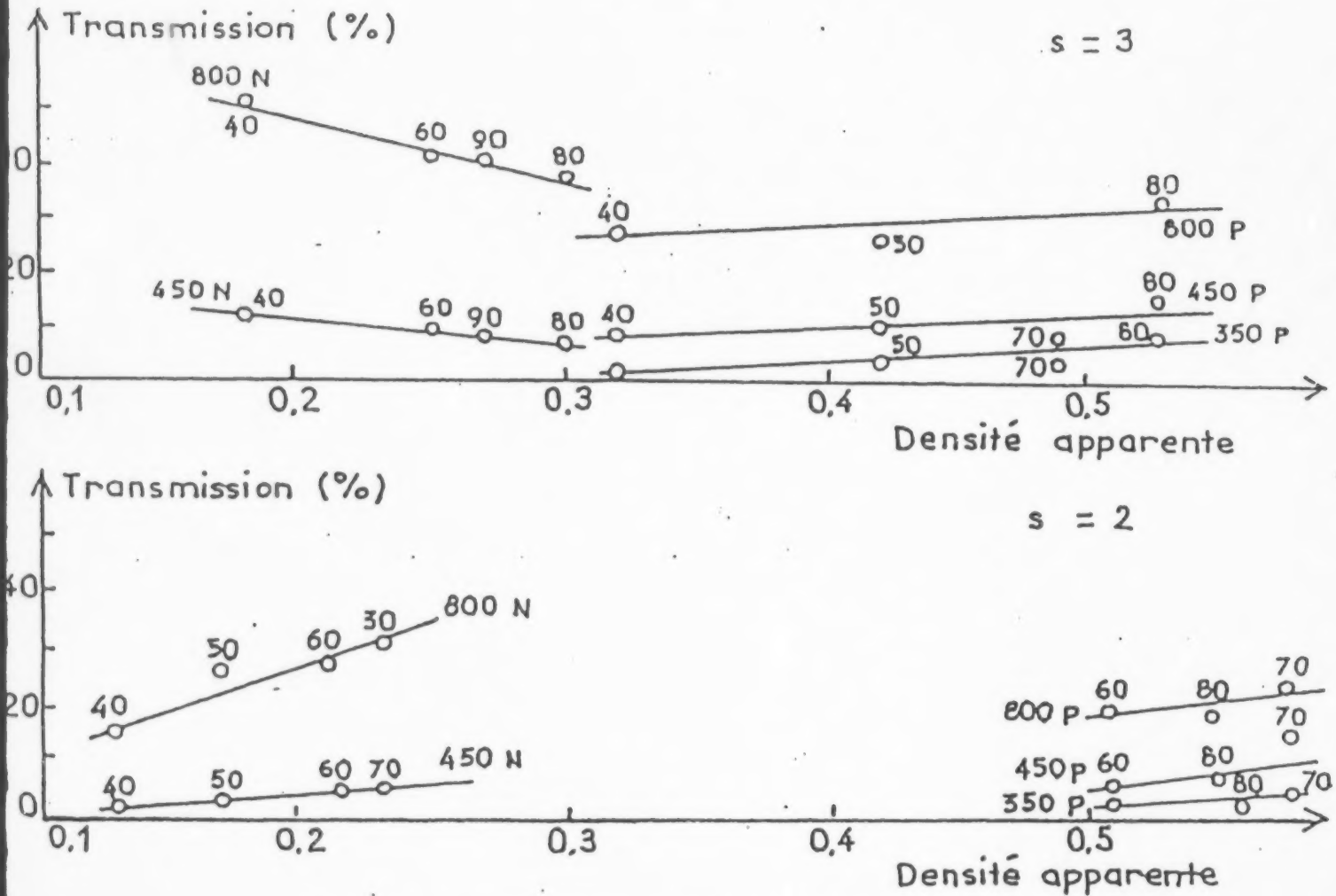


Fig. IC(i) - The transmission of silica aerogels at 3 wavelengths, 350, 450, and 800 nm, as a function of S, the ratio of moles of water to moles of methyorthosilicate, and the resultant density. Hydrolysis conditions: N = ammonia, P = neutral. (14) For s = 2, and s = 3.

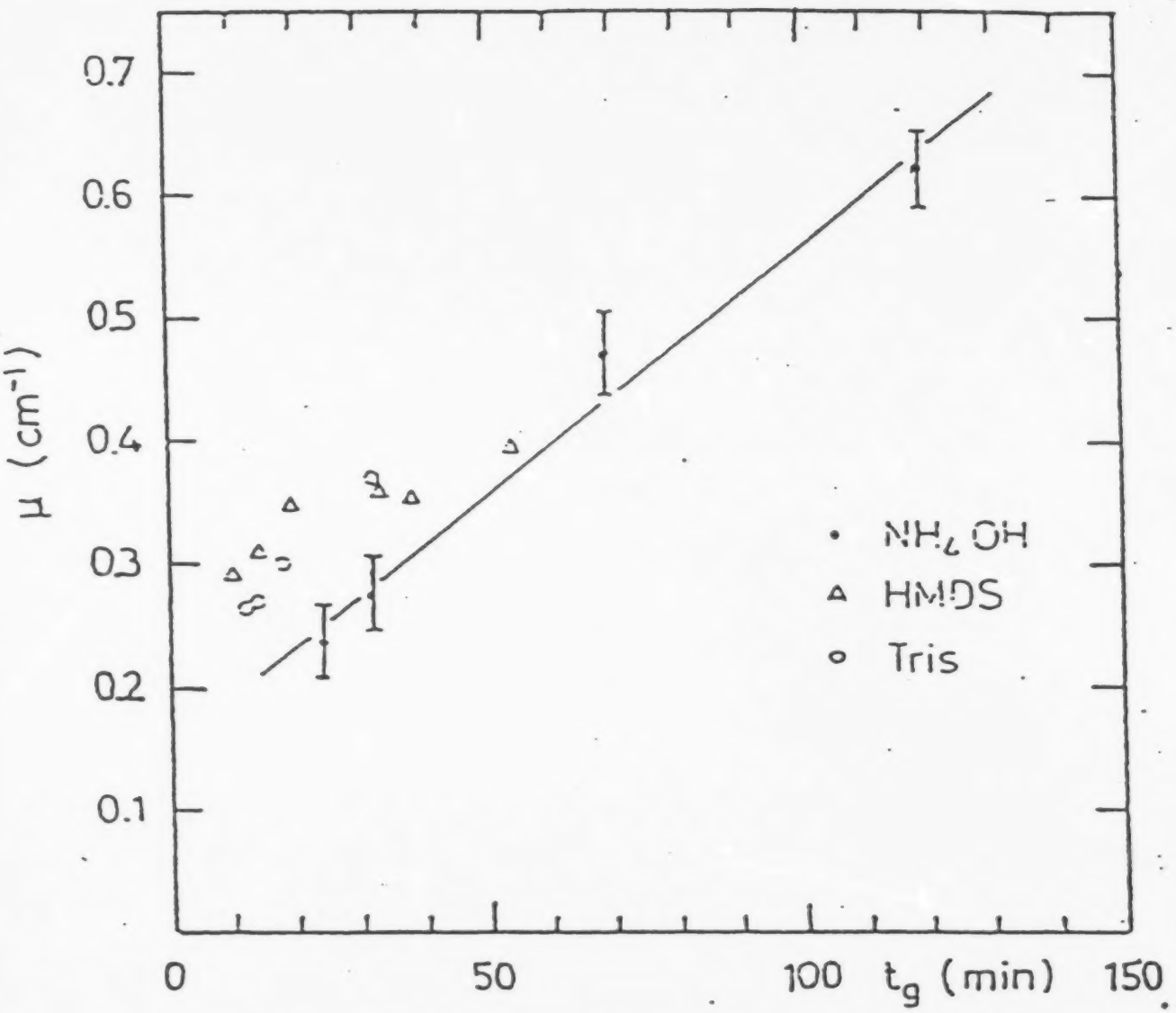


Fig. 2. - Transmission coefficient of aerogel samples fabricated with different gelling times t_g and measured with blue light (= 438 nm). The relative volumes were silan: water: methanol = 2 : 1 : 4.7. The straight line represents the points with ammonia as catalyst. The data points for HMDS and Tris have similar errors as for ammonia. (16).

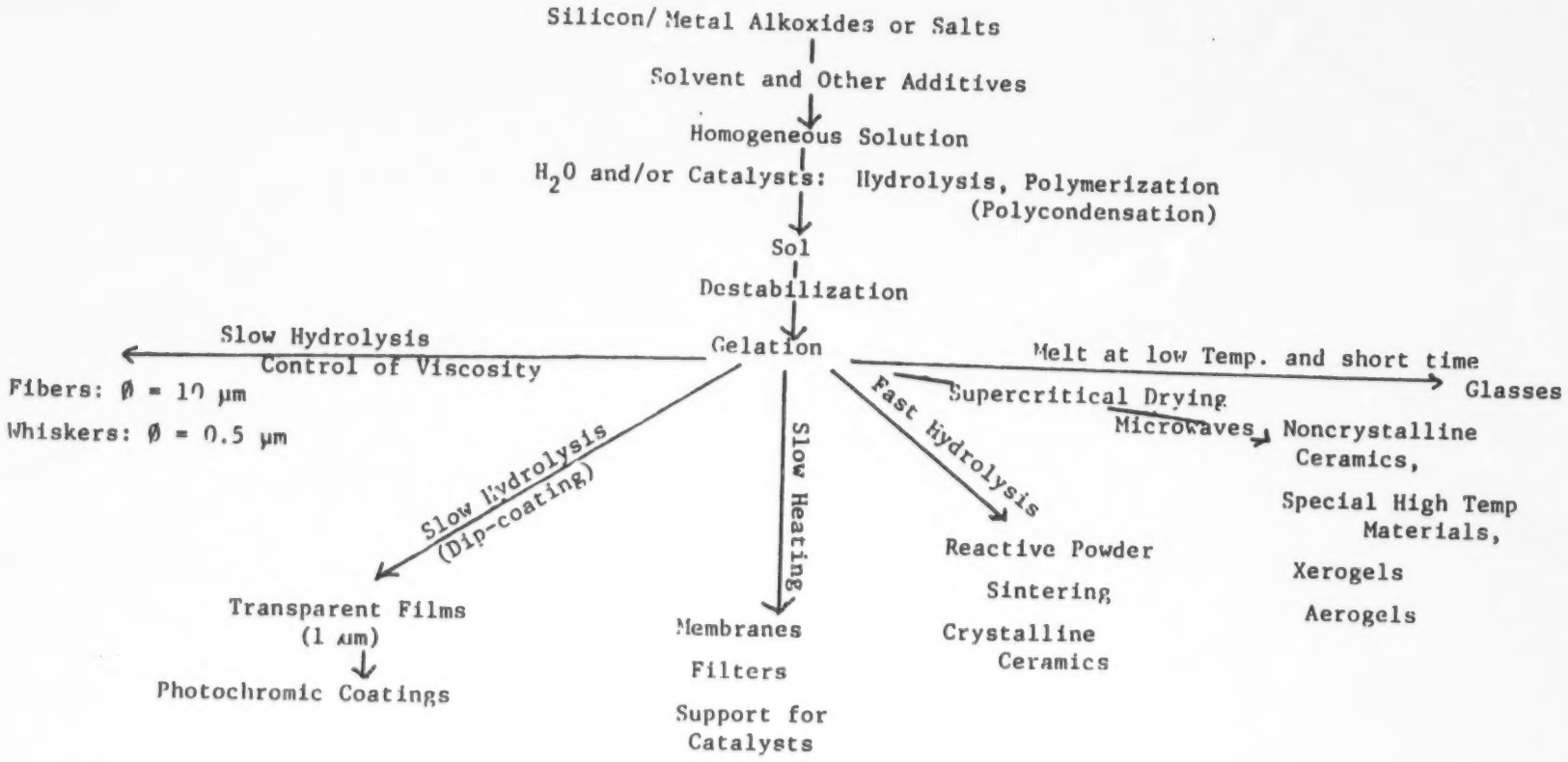


Fig. 3. The Sol-Gel Process

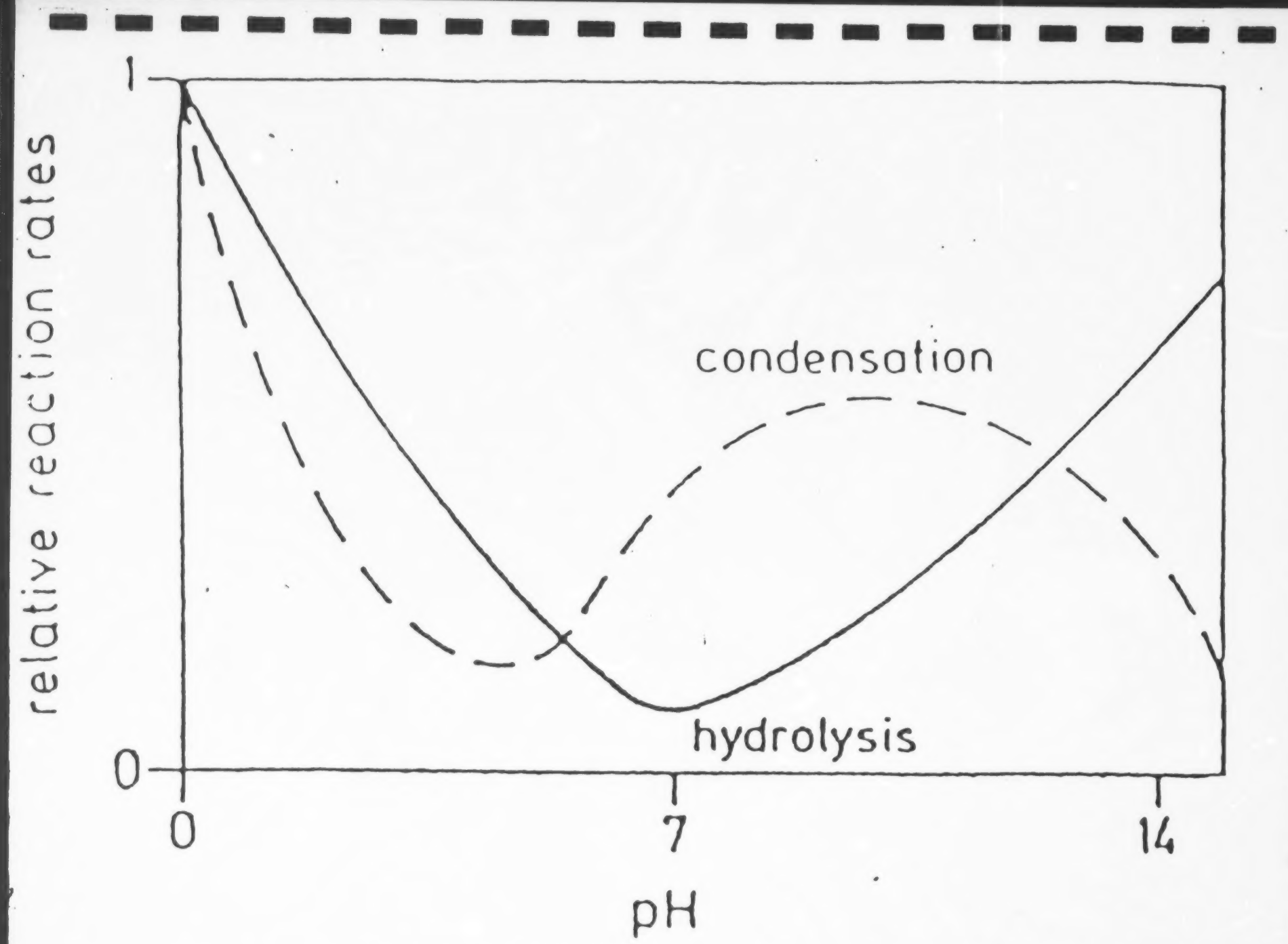


Fig. 4. - Hydrolysis and condensation of TEOS as a function of pH, according to [17].

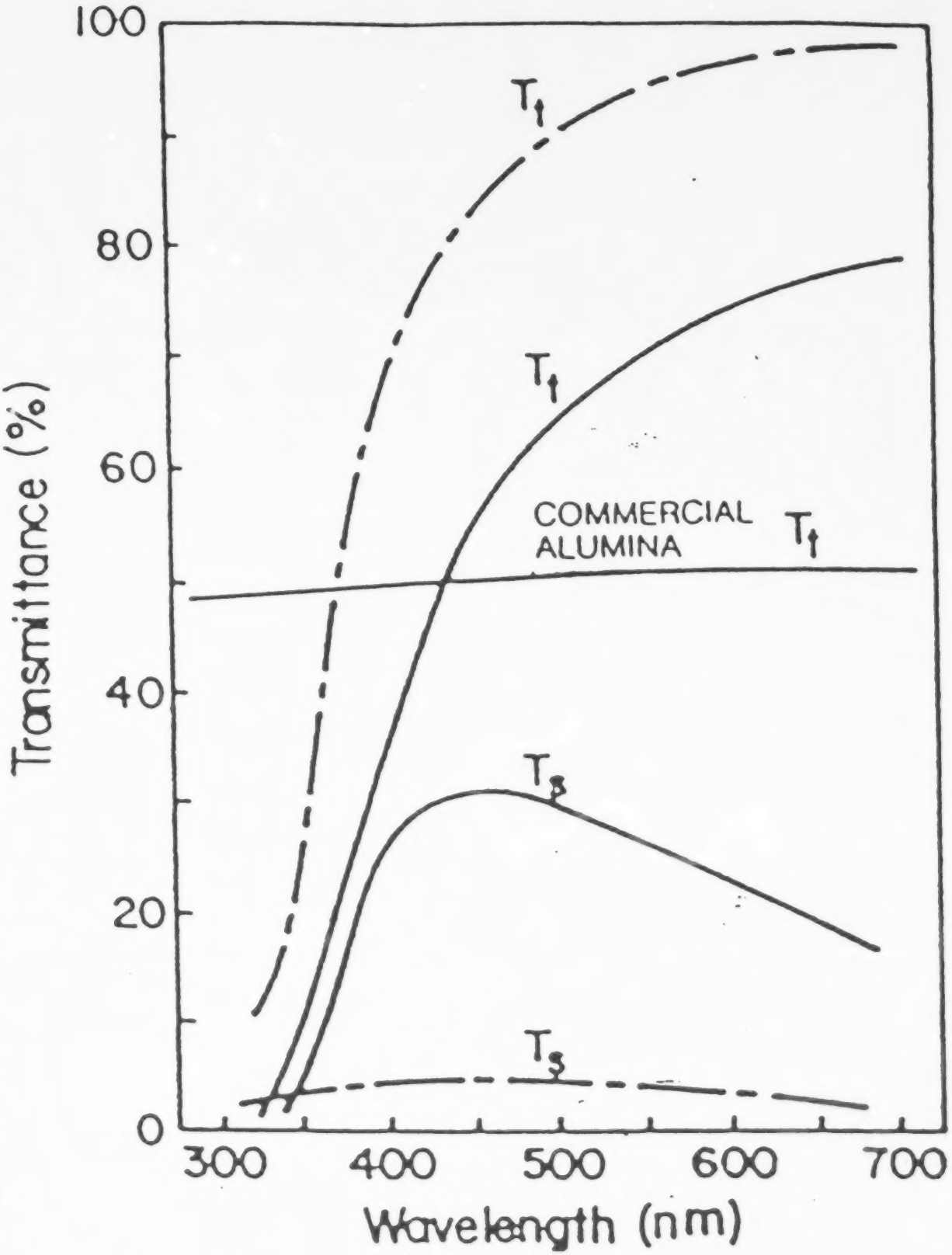


Fig. 5. - Total (T_t) and scattered (T_s) transmittance of specimen 2 mm thick. Solid line represents dry stage, dash-dot line water-impregnated condition. Also shown is T_t of a dense transparent commercial alumina [illegible]

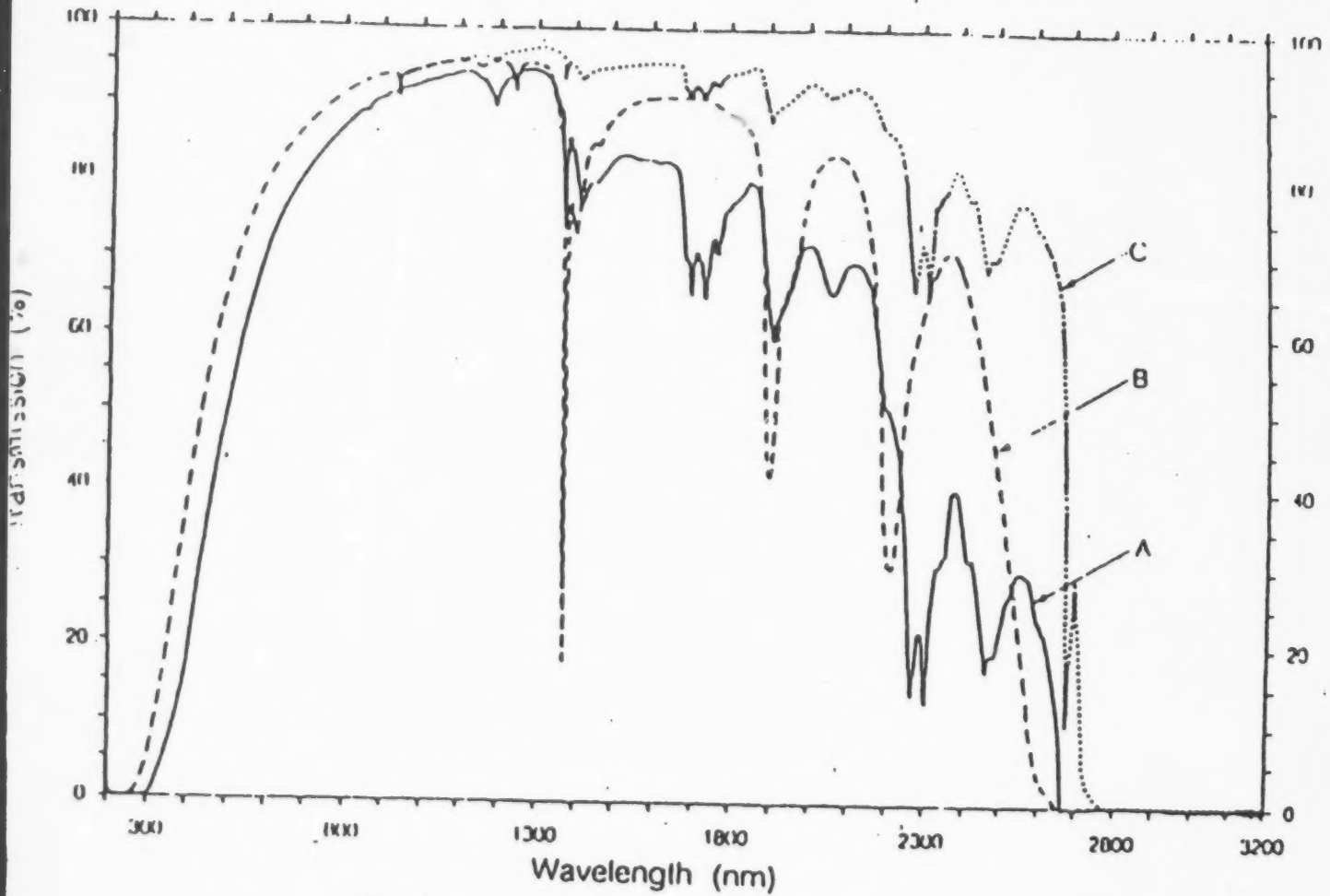


Fig. 6. - Transmission spectrum of (A) base catalyzed aerogel (4 mm thick) prepared by CO_2 supercritical drying: (B) the spectrum after the sample was heated in air at 250°C for 4 hours; (C) the spectrum after the sample was heated to 500°C for 12 hours. (Curve C not drawn below 600 nm because of clarity but follows closely curve B in this region). (45).

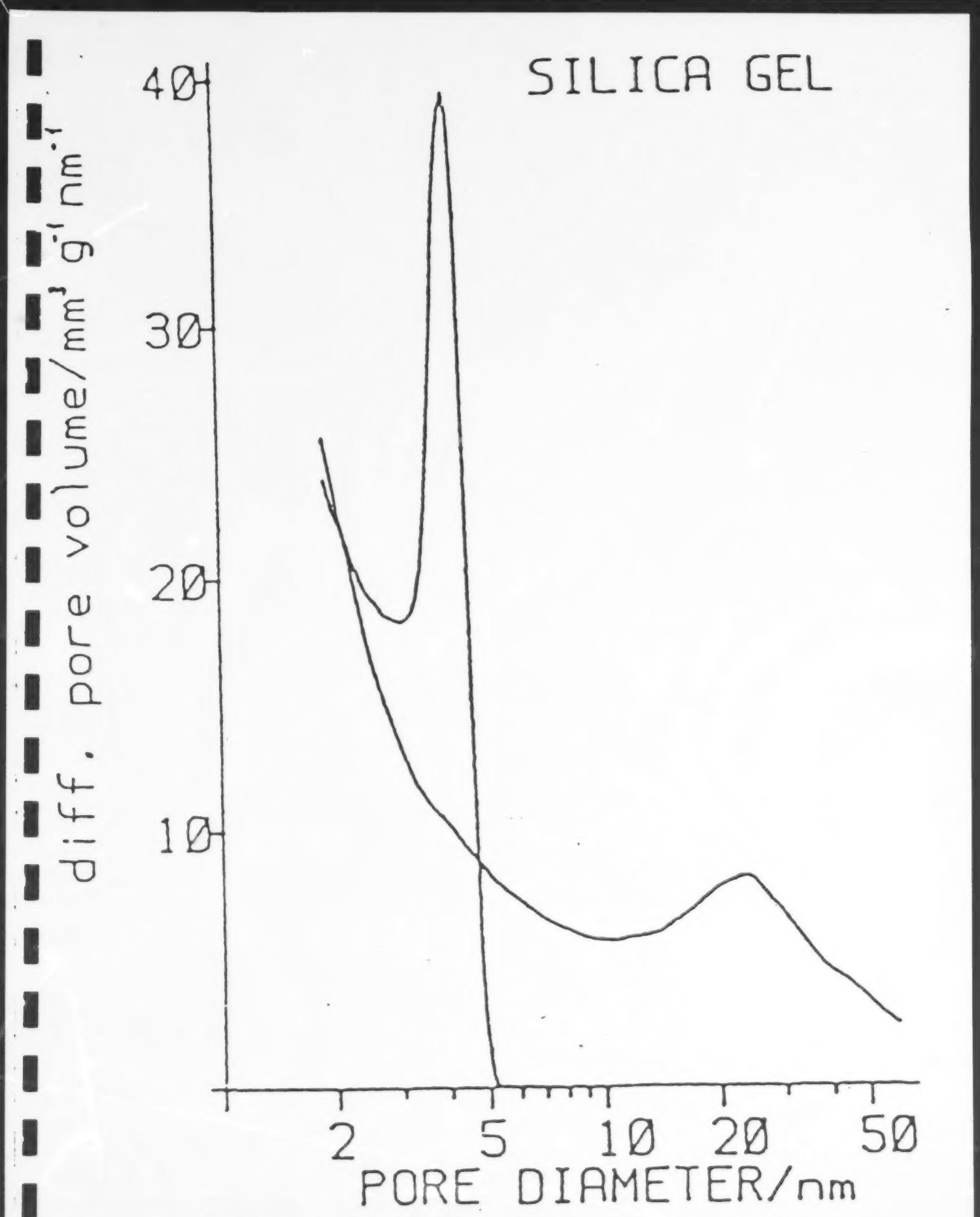


Fig. 7a. - Pore size distribution for silica gel with will-defined

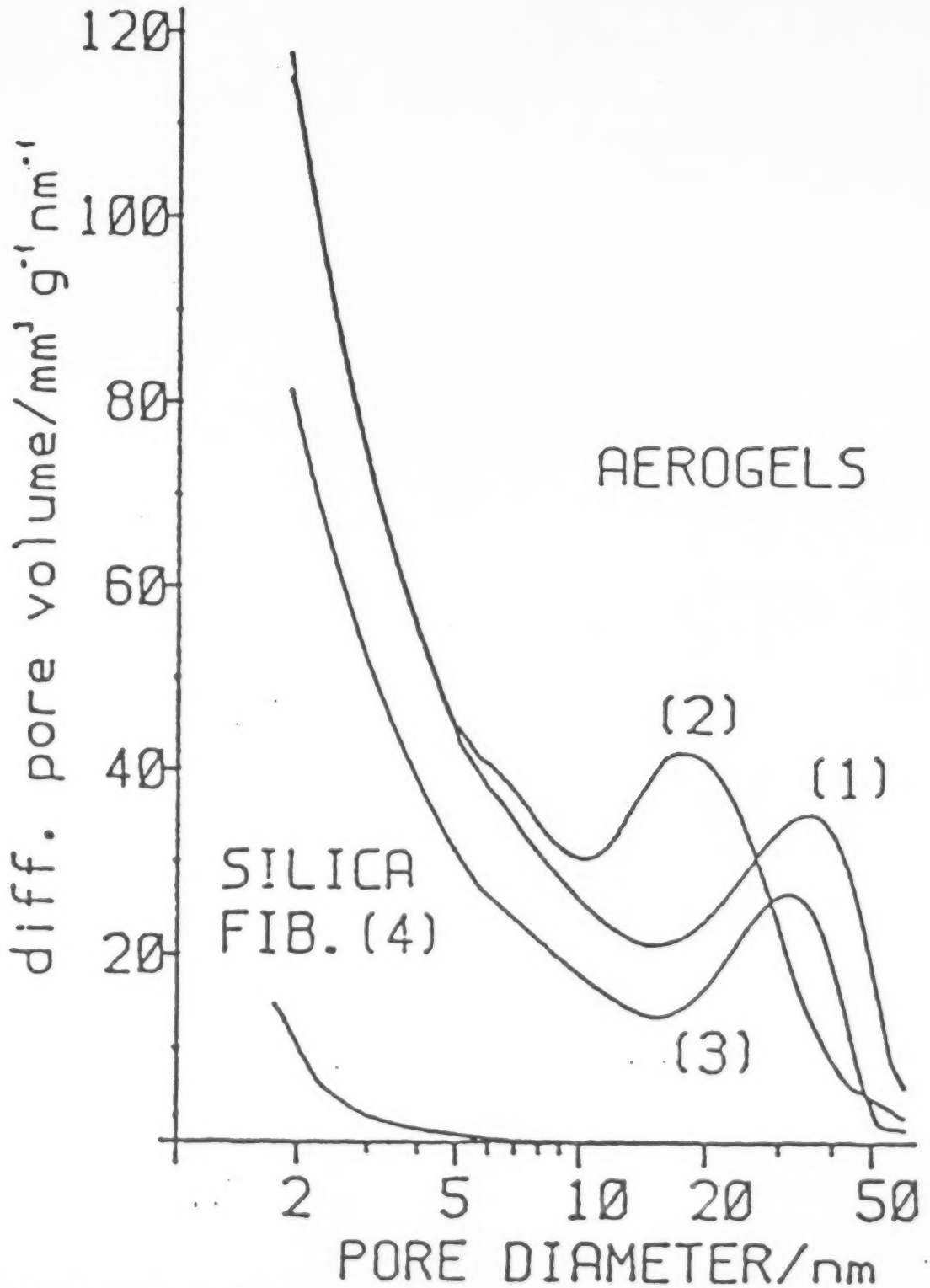


Fig. 7b. - Pore size distribution for aerogel (samples 1, 2, 3) and for silica fiber (57).

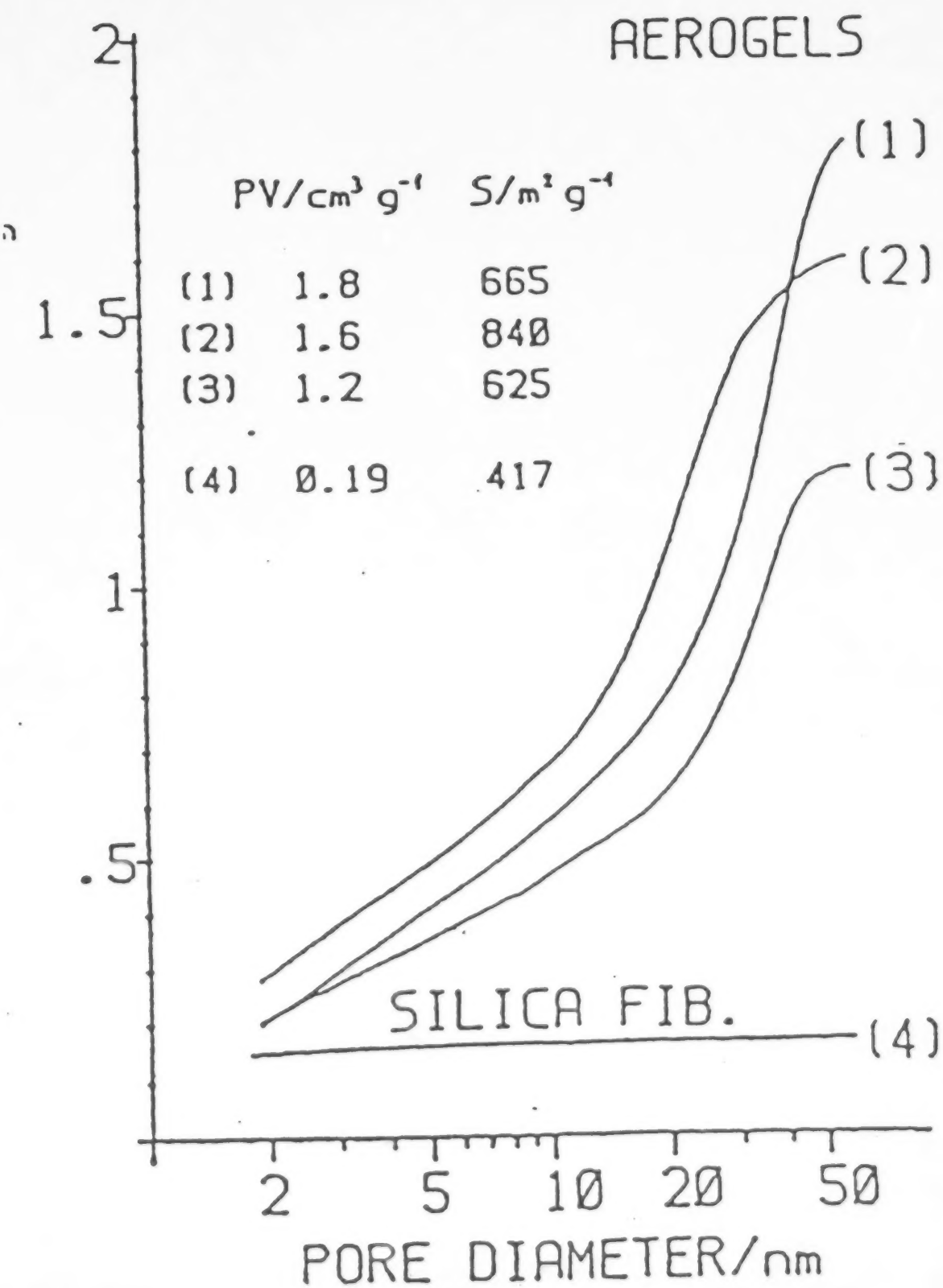
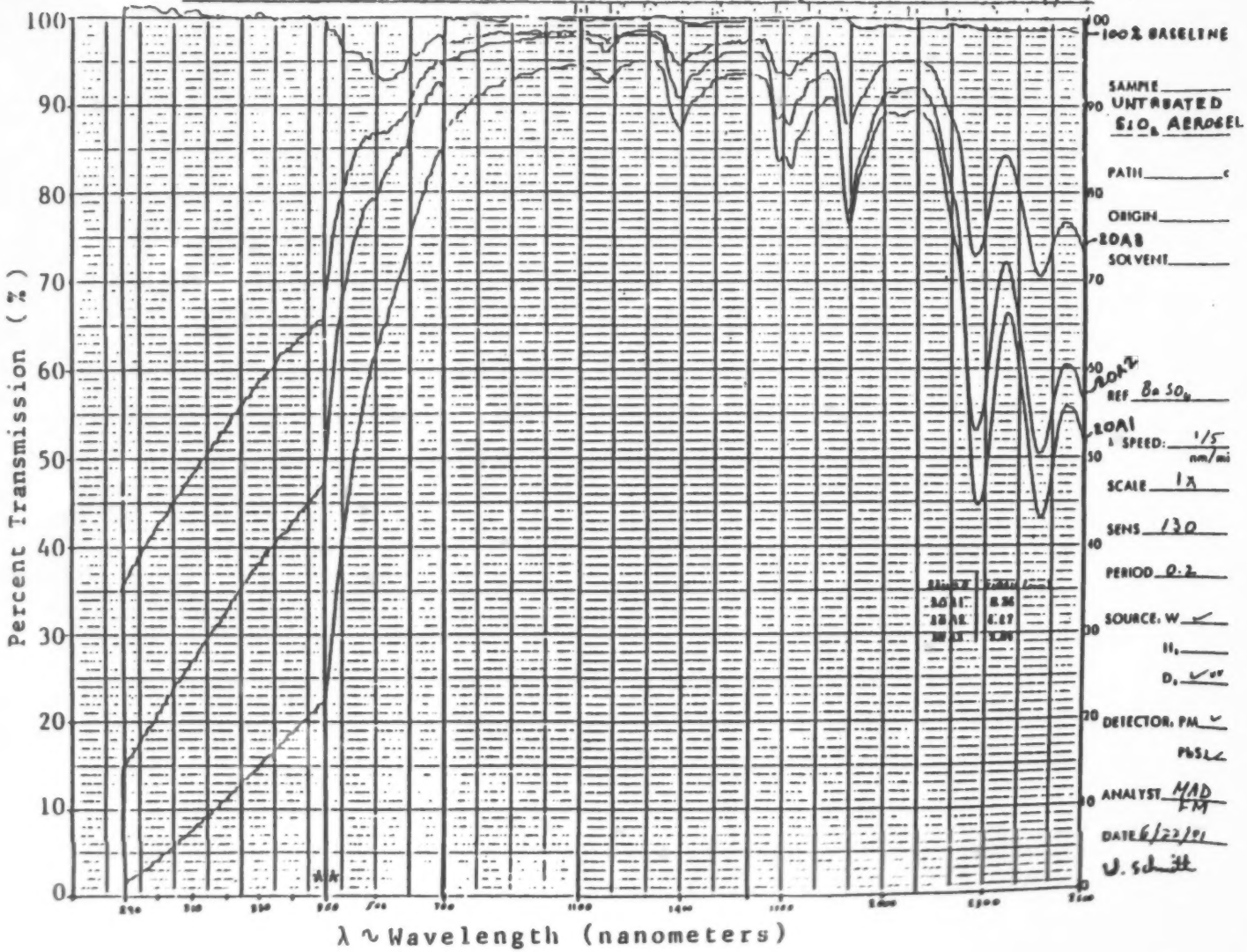


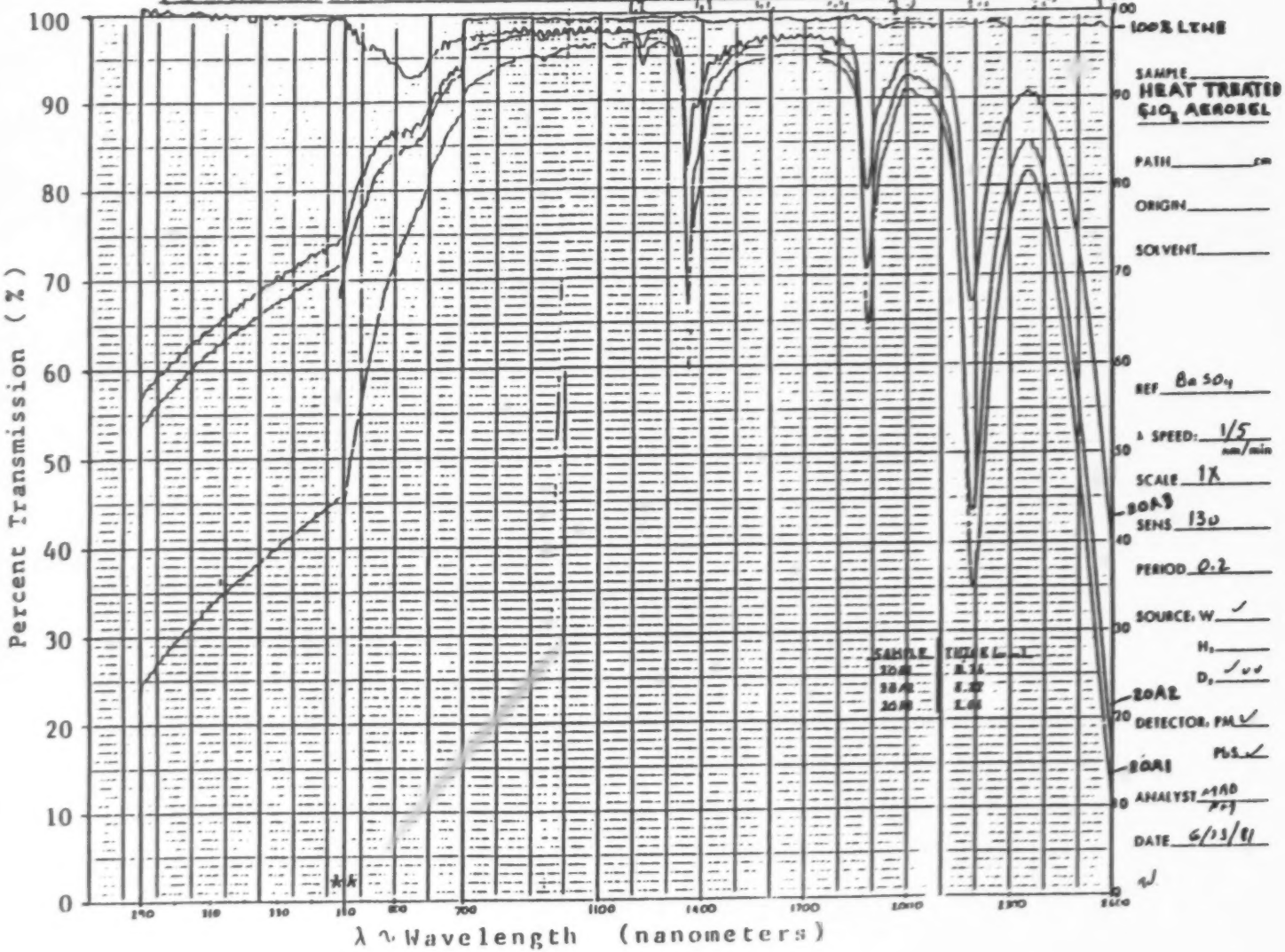
Fig. 7c. - Cumulated pore volume represented by Adsorbed liquid N_2 volume per sample mass for aerogels (1, 2, 3) and silica fiber (57).

FIGURE 8a. Visible Transmission Spectra of Aerogel*



* Scale changes at 350 nm.

FIGURE 8 b. Visible Transmission Spectra of Aerogel (-1).



*Scale changes at 350 nm.

TABLE 1

Compressive Strength of Aerogel (4)

Sample	Area (m^2)	Initial Thick. (mm.)	Linear Region			End of Test	
			σ_{max} (N/m^2)	σ_{max} (psi)	E (N/m^2)	σ_{max} (N/m^2)	σ_{max} (psi)
C1	1.145×10^{-3}	4.21	7.69×10^5	112.	2.00×10^6	6.99×10^6	1010.
C2	3.360×10^{-4}	2.87	1.49×10^6	216.	2.18×10^6	2.38×10^7	3450.
		Average →	1.13×10^6	164.	2.09×10^6		

TABLE 2

Tensile Strength of Aerogel (4)

Sample	Area Break (m^2)	Ultimate Force (N)	σ_{max} (N/m^2)	σ_{max} (psi)
T1	9.61×10^{-5}	0.440	4580.	0.66
T2	2.13×10^{-4}	2.675	12540.	1.82
		Average →	8560.	1.24

Table 3. Apparent density ρ_a, true density (density of skeleton) ρ_t, specific pore volume v_p and porosity Π for different aerogels. (59)

Sample	$\rho_a/(g \cdot cm^{-3})$	$\rho_t/(g \cdot cm^{-3})$	$v_p/(cm^3 \cdot g^{-1})$	Π / %
1	0.133	2.44	7.11	94.5
2	0.205	1.87	4.34	89.0
3	0.240	1.99	3.66	88.0
4	0.230	2.09	3.86	88.5
5	0.287	1.93	2.97	85.1

pellets

TABLE 4A

Steady-State Thermal Conductivities (4)

Run	Remarks	T_h (°C)	T_c (°C)	k ($\frac{BTU}{hr \cdot ft \cdot °F}$)	k ($\frac{W}{m \cdot K}$)	k_{avg} ($\frac{BTU}{hr \cdot ft \cdot °F}$)
1a	Expt. 1 6/80	98.8	19.7	0.0275	0.0476	
1b	ρ= 0.119 g/cm^3 Δx= 10.05 mm	98.7	20.0	0.0308	0.0533	0.0301
1c	A= 25.83 cm^2	98.6	21.8	0.0321	0.0556	
2a	Expt. 2 6/81	88.8	35.6	0.0580	0.1004	
2b	ρ= 0.14 g/cm^3 Δx= 8.05 mm	94.5	37.8	0.0250	0.0433	0.0454
2c	A= 25.02 cm^2	92.8	37.9	0.0533	0.0922	

TABLE 48

Unsteady-State Thermal Conductivities (4)

Run	Time (sec.)	T_{h1}(°F)	T_{h2}(°F)	T_{mid}(°F)	k ($\frac{BTU}{hr \cdot ft \cdot °F}$)
1	0.0	83.2	83.5	83.2	-
	83.	139	134	123	0.0043
	173.	142	146	139	0.0041
	263.	147	144	143	0.0041
2	0.0	82	84	82	-
	32	110	123	105	0.0040
	122	147	143	136	0.0045
	212	150	150	147.5	0.0052

avg. $k_1 = 0.0041$

avg. $k_2 = 0.0045$

TABLE 4C

Results of the Aerogel Window Steady-State Thermal Testing (4)

Run	Internal pressure (mm. Hg)	T_{hb} (°F)	T_{cb} (°F)	T_{hl} (°F)	T_{cl} (°F)	Mass of cold air (lb.mol/hr.)	Aerogel k ($\frac{BTU}{hr \cdot ft \cdot °F}$)	Window U_o ($\frac{BTU}{hr \cdot ft^2 \cdot °F}$)	R factor ($\frac{hr \cdot ft^2 \cdot °F}{BTU}$)
1	744.	171	118	106	86.0	2.154×10^{-3}	8.86×10^{-4}	0.0275	36.4
2	743.	171	112	108	86.0	2.006×10^{-3}	7.30×10^{-4}	0.0217	46.0
						average→	8.08×10^{-4}	0.0246	40.6
3	600	172	114	109	86.9	1.593×10^{-3}	4.63×10^{-4}	0.0144	69.5
4	596	172	111	110	85.5	1.534×10^{-3}	3.93×10^{-4}	0.0128	77.8
						average→	4.28×10^{-4}	0.0136	73.5

T_{hb} = well mixed temp. of hot side air

T_{cb} = well mixed temp. of cold side air

T_{hl} = thermocouple temp. of hot glass surface

T_{cl} = thermocouple temp. of cold glass surface

TABLE 5a

Literature Values of the Thermal Conductivity (4, 209)

Powder	Remarks	Density ($lb./ft^3$)	Gas Pressure (mm Hg)	Interstitial gas	Conductivity[b] (BTU/hr·ft·°F)	Conductivity (W/m·K)
Silica aerogel	Chemically Prepared (250 Å)	6.2	10^{-4}	-	12×10^{-4}	21×10^{-4}
		6.2	628[a]	N_2	113×10^{-4}	196×10^{-4}
		6.2	628	He	358×10^{-4}	620×10^{-4}
		6.2	628	H_2	462×10^{-4}	800×10^{-4}

[a] Barometric Pressure at Boulder, Co.

[b] 1 in. sample thickness, boundary temp. of 804 and -323 °F.

TABLE 5b

Literature Conductivities (4, 88)

AIR		CO_2		CCl_2F_2	
Press. (mm)	Conduc.[b] $\times10^5$	Press. (mm)	Conduc. $\times10^5$	Press. (mm)	Conduc. $\times10^5$
740	4.85	745	4.33	740	3.71
387	4.06	397	3.84	406	3.38
206	3.61	206	3.42	259	3.18
183	3.63	100	3.06	123	2.86
94	3.26	49	2.98	59	2.63

[b] Conductivities in cal/cm·sec

Table 6a

Experimental Data on the Densification SiO_2 gels (14 4)

GEL	temperature (°C)	gel density (g/cm^3)	specific surface area (m^2/g)	particle diameter *) (nm)
1	300	0.16	740	8
2	800	0.16	780	8
3	1150	0.27	530	11
4	1200	0.66	160	12
5	1210	1.00	76	24
6	1225	1.41	36	40
7	1250	2.08	–	–

*) approximate diameter of the particles as derived from the TEM pictures

TABLE 6b

Initial N_2 Pressure and Corresponding Density and Shrinkage of a Gel (144)

N_2 pressure (bar)	specific density (g/cm^3)	shrinkage (%)
0	0.49	73 (cracked)
10	0.27	52
40	0.14	7
80	0.13	0

Table 6c
Experimental Data of Low-Density Gels (144)

GEL	gel density (g/cm^3)	particle diameter (nm) *)	specific surface area (m^2/g)	sphere density (g/cm^3) **)
1	0.15	20	520	0.38
2	0.05	10	1080	0.37
3	0.03	8	1590	0.31

*) approximate diameter of the particles as derived from the TEM pictures

**) calculated from the specific surface area and particle diameter measurements taking into account the degree of interconnection of the particles